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A BRIEF COURSE

IN

QUALITATIVE CHEMICAL ANALYSIS

FOR SCHOOLS AND COLLEGES

BY

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PREFACE.

In the whole province of chemistry there is no branch that so strongly appeals to the student's interest and so completely enlists his efforts as that of qualitative analysis. The discovery of scientific truth and the conscious mastery of definite problems will ever be a source of joy to the majority of normal minds. Qualitative analysis abounds in such problems. Their solution not only affords the keenest delight and satisfaction, but provides at the same time the soundest kind of training in the use of those three great instruments for the ascertainment of truth, — experimentation, observation, and inductive reasoning. These considerations would seem to furnish a sufficient motive for a thorough study of this branch of science, even if it lacked the practical value which it really possesses for the professional analyst.

Until within recent years, this subject was considered rather too abstruse and too intricate for any but the technical student, and this is not surprising when we take into account the distracting method by which it was formerly presented in our colleges and universities. Educators, however, are coming to understand that for the sake of mental discipline and for the purpose of establishing a scientific habit of thought and work, it is quite unnecessary to master a treatise or to attain to a high degree of specialization. There are certain fundamental principles forming the basic structure of every science, whose understanding depends upon the actual knowledge and correlation of relatively few facts or phenomena. Indeed, it is frequently the case that a multiplicity of detail, presented before the apprehension of principles and laws, is bewildering and harmful rather than of substantial benefit.

In arranging an introductory course in qualitative analysis, it devolves upon one to select such material as will most clearly and positively illustrate types of chemical changes, and which may therefore be used as a scientific basis for generalization. The presentation of this material must be orderly and systematic, so that the student is led irresistibly to the recognition of relationship and of logical sequence. Happily, the subject is one that lends itself readily to this method of procedure through its utility in the analytical processes; so readily, in fact, that the student is liable to overestimate its value as an art and slight its scientific aspect. If, however, while stimulating an interest in the analytical processes, attention is enforced to the *rationale* of the subject, qualitative analysis becomes a most valuable means of teaching chemical truth, and is unsurpassed as a drill in the methods of experimental investigation.

The present work is an effort to embody the writer's views of a thoroughly practical introductory course, suitable for the needs of the general student as well as of those who intend to become professional analysts. In fact, he is convinced that the training best suited to the one is equally well adapted to the other, and that if qualitative analysis is to be pursued at all, the initial work should be done in the same way and along the same lines by all classes of students.

The book was designed primarily to facilitate the giving of class-room instruction under the author's supervision, and has been so used for the past five years. Its sole claim to originality is in the selection and arrangement of the subject matter. The schemes of separation and the tests employed are those in common use, and are taken largely from such well-known authorities as the works of Fresenius, Prescott and Johnson, and Watt's Dictionary.

In its general features the plan of the book is inductive, with such suggestions and safeguards as seem necessary to avoid dissipation of time and of energy. In truth, a strictly inductive presentation of qualitative analysis is beyond the compass of the ordinary scientific worker. There are so many modifying influences, and the conditions for success are so exacting, that the rediscovery of all necessary factors is as impracticable as it is unnecessary. *Some* facts, therefore, must be taken by the student on trust, though in a large measure subject to verification in the subsequent part of the course.

It is in the treatment of basic analysis that this work differs most noticeably from its predecessors. Not only are the salts of each metal first treated separately with the reagents essential to the analytical processes, but the reagents are all introduced successively, in the same order, and, as near as may be, under the same conditions that prevail in systematic analysis. The student thus becomes familiar with the most characteristic reactions under such circumstances as will impress their real value in the schemes of separation and grouping.

It will be seen by reference to the text that each experiment in Part I. is in a measure a review of all the preceding experiments. This is made possible by a system of references which serves three important purposes; viz., it lessens the text fully one-third by avoiding all repetition in the instructions; it emphasizes the similarity in the treatment of many metals up to the point of separation, and thus makes clear the plan upon which grouping and subsequent differentiation are based; and, finally, the review unifies and clarifies the whole subject in the pupil's mind, rendering superfluous and unnecessary all formal analytical tables and skeleton outlines. So far as practicable, the same plan is pursued in acid analysis, although it has a more limited application, owing to the impossibility of grouping the acids with the same precision as the metals.

In Part III. the author has endeavored to simplify and systematize the steps to be taken in the full examination and determination of unknown substances. While by no means of universal application, the system adopted is sufficiently comprehensive to insure the identification of the metals and acids embraced within the scope of this manual.

The time available for the study of this subject will determine to what extent it is advisable to use the Supplementary Exercises. They have no direct relation to the schemes of analysis, and may be omitted without interfering with the symmetry of the course. Their use, however, will greatly enlarge the horizon and power of the student, and help to develop a habit of independent practice and investigation.

While no effort has been spared to insure accuracy in every detail of the work, the author cannot hope to have eliminated all errors. Corrections and suggestions by fellow-workers will be freely welcomed.

In conclusion, the author wishes to express his appreciation of the generous assistance rendered by Professor Wilber D. Engle, of the University of Denver, Mr. John L. Sammis, of the University of Illinois, and Mr. Harry V. Kepner, of the Denver Manual Training High School, whose helpful suggestions and kindly criticisms are reflected in many important details of the book.

DENVER, COLORADO,
May 1, 1902.

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QUALITATIVE ANALYSIS.

INTRODUCTION.

Qualitative Analysis is that branch of chemistry which includes all processes by which the constituents of a substance are determined. It embraces two fairly distinct classes of operations, — those *in the dry way* and those *in the wet way*.

Analysis *in the dry way* is dependent upon the deportment of solid substances at a high temperature, as their fusibility, volatility, oxidizing or reducing power, etc. Aside from its use in determinative mineralogy and assaying, it is limited to the preliminary examination of substances in the systematic course of qualitative analysis.

We are concerned here chiefly with operations *in the wet way*. These require that the material be in solution, and consist in bringing about chemical changes, or *reactions*, through contact with known substances called *reagents*. Those reactions which result in the formation of *precipitates*, *i.e.* solids insoluble in the medium present, are by far the most important resources of chemical analysis. It is the business of the analyst to know how to induce such changes, as well as to interpret their results, and to this end he must possess a thorough knowledge of the elements themselves and of their most important compounds. Although the detection of the elements is the ultimate object of analysis, it is seldom that they are obtained in their uncombined condition; nor is it at all necessary to their identification that they should be so obtained. If, as the result of a series of operations upon an unknown substance, some compound of known composition and properties is formed, as, for instance, silver chloride, the analyst is as positive that silver is present as if the metal itself had been extracted.

PRELIMINARY KNOWLEDGE AND TRAINING.

It will be readily understood that for the successful pursuit of this study the student should have sufficient knowledge of general chemistry to understand clearly the object of the various analytical operations and the nature of the main reactions. Without this equipment on the part of the student, and a constant readiness in the interpretation of phenomena, the experiments degenerate into purely empirical processes, which have but little educational or scientific value.

While it is not necessary that a student should have had experience in chemical preparations and manipulations, it is by all means desirable. Qualitative analysis is an art as well as a science, and knowledge will be found of little worth without the practical skill and ability that come of painstaking experience.

CHEMICAL OPERATIONS.

The operations and processes employed in qualitative analysis are in the main simple and easily understood. In the following descriptions and suggestions only such information is given as is of general application, more detailed instruction being reserved for the individual experiments. In the presentation of this topic, nothing can take the place of illustration and demonstration on the part of the instructor, whose efforts this manual can merely supplement and strengthen.

Solution. — The first condition essential to operations *in the wet way* is that of solution. In fact, it is upon this property of substances that the whole framework of analysis rests. In its popular sense, the term *solution* is used to denote a homogeneous liquid mixture, in which the substance dissolved retains its original chemical properties, and from which it can be separated by evaporation. If the action of the solvent results in the formation of new substances, the liquid is then termed a *chemical solution,* although it is properly chemical action *and* solution.*

The most important and the almost universal solvent is water. It could no more be dispensed with in analytical operations than the vessel which contains it, although it is seldom taken into account in considering the chemical changes. Some other simple solvents are alcohol, ether, and carbon disulphide. While there is probably no such thing as absolute solubility or insolubility, regardless of proportions, the degrees of solubility vary within limits so wide as to furnish a basis of operations for the practical separation of substances. Heat usually accelerates the solution of solids, and increases the capacity of the liquid to act as a solvent. For example, while 1 cc. of water at 15° C. will dissolve only one-fourteenth of a gram of mercuric chloride, at 100° C. it will dissolve one-half a gram.

Evaporation is a process by which liquids or gases are separated from less volatile or from fixed bodies. It is due to the application of heat, strong at first, but diminished toward the close. Its usual object is to recover solid matter from solutions without chemical change. Since many solids are volatilized or decomposed at a temperature but little above that of boiling water, the operation should be watched closely in order to avoid loss. In fact, it is seldom safe to evaporate to dryness over a naked flame; but instead the process should be conducted over a steam-bath or a sand-bath, or at least an iron plate.

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* For a brief statement of the now generally accepted dissociation theory and its *bearing upon the* phenomena of solution, see Appendix E.

Precipitation. — Unless otherwise directed, reagents should be added *drop* by *drop*, with constant stirring. Sometimes a single drop is sufficient to produce the desired effect. If a precipitate forms that is to be separated from the solution, the reagent must be added until the precipitation is complete. Unless this is done, the subsequent treatment of the solution may lead to false indications and failure. On the other hand, any considerable excess of a reagent must be guarded against, since many precipitates are soluble in the reagents that produce them. As a rule, precipitation takes place most readily and completely in a hot and fairly concentrated solution, and is favored by shaking or stirring. The time required for complete precipitation varies widely, from a few minutes to a whole day. Usually, five or ten minutes will be found sufficient.

Filtration is a process by which liquids are mechanically separated from the solids which they hold in suspension. It is performed, ordinarily, by pouring the substance to be filtered over a piece of unsized paper arranged in a glass funnel; the liquid trickles through, while the solid particles are retained on the *filter*. Whenever permissible, the liquid should be filtered hot, since the filtration then takes place much more rapidly. The operation is also greatly facilitated by prolonging the funnel tube to a length of ten or twelve inches. This can be most easily done by attaching a piece of glass tubing of small diameter, the upper end of which should be contracted by fusion to about one-sixteenth of an inch bore.

If subsequent operations require that the precipitate be dissolved, it must be washed thoroughly by successive additions of water in order to free it as completely as possible from all clinging soluble substances. There is no safe plan except to continue the washing until appropriate tests show that the wash-water is freed from the liquid in which the precipitate was formed.

Decantation. — If the precipitate is granular and settles readily, it is often advantageous to combine *decantation* with filtration. This is done by first pouring off the supernatant liquid upon a filter, and then washing the precipitate by repeatedly adding and pouring off small portions of water. Finally, the precipitate may be removed to the filter, and the washing finished there, if necessary. In the case of gelatinous precipitates, which clog the pores of the paper and retard filtration, decantation is almost indispensable.

In dissolving precipitates, use no more of the solvent than is necessary, in order that the resulting solution may be nearly if not quite saturated. If the precipitate is to be dissolved on the filter, this process is best accomplished by repeatedly passing the same portion of the solvent through the paper. Precipitates may be removed from the filter, if necessary, either by means of a spatula or by washing them with a small stream of water through a puncture made in the point of the filter.

GENERAL DIRECTIONS.

Every possible precaution should be taken to guard the reagents from contamination. To this end, the stopper of a reagent bottle must not be laid down while the reagent is being used, and should invariably be replaced in the bottle to which it belongs. Excess of a reagent is never to be returned to the bottle, and it is seldom advisable to attempt to save it.

Neatness and cleanliness in the care of the desk, apparatus, and supplies are indispensable to success in qualitative analysis. The student should provide himself with a test-tube brush and plenty of clean cloths and towels, and should use them freely. As Sir Henry Roscoe expresses it, "Those who work in a mess not infrequently get their minds in a muddle."

Before beginning an experiment the student should read over the full set of instructions with the utmost care, in order to secure a comprehensive grasp of the operations. Especially should he give close attention to the accompanying notes and suggestions, for they will help to clear away many difficulties and insure an intelligent and trustworthy procedure.

One of the strongest evidences of thorough work is a neat, concise, and accurate record. It should stand for real experience and observation, and is of value only when made at the time the experiment is performed. Such a record serves three important purposes: It emphasizes the necessity of observing carefully everything that takes place; it crystallizes the ideas of the student into genuine knowledge by requiring brief but exact expression of results; and finally, it furnishes a most valuable storehouse of information without which it is practically impossible for the student to analyze unknown substances.

ORDER OF STUDY.

The subject as presented in this manual is treated in three parts or divisions: The first part consists of a series of experiments to illustrate the properties of the bases and the methods by which they may be separated and detected, while the second part deals with a similar treatment and study of the more common acids. This initiatory work is necessarily done on known solutions, and requires the most painstaking and conscientious study. No step in the whole series of operations should be allowed to go unchallenged, nor should there be the slightest doubt as to the occurrence of any phenomenon or of its significance in the interpretation of results. Failure is often due to seeming trifles, to a lack of some condition that would be just sufficient to turn the balance; and one of the earliest and most valuable lessons to be learned by the student of this science is that the laws governing chemical changes are fixed and immutable, and subject neither to caprice nor circumvention.

Not until after he has become thoroughly familiar with Parts I. and II. is the student prepared to take up the systematic examination of unknown substances, which is the province of the third division of the manual.

USE OF AUTHORITIES.

The diligent student will not rest content with the results of his own experimental demonstrations and investigations. The science of chemistry, as it is known to-day, is the fruit of many generations of patient toil and research, and it is only by taking advantage of this great stock of accumulated knowledge that one can hope to secure a real mastery of the subject. A constant reference to authorities should be one of the most important features of laboratory training. No amount of individual experience can take the place of it. It serves to confirm or to correct one's own judgment, and brings one at the same time into personal relations and sympathy with those eminent investigators whose names are interwoven with the history of the science. Every laboratory, therefore, should have its working library. It may be large or small, according to means; but let there be something. Start with such standard works as Roscoe and Schorlemmer's Treatise on Chemistry, Fresenius's Manual of Qualitative Chemical Analysis, Prescott and Johnson's Qualitative Chemical Analysis, Ostwald's Foundations of Analytical Chemistry, and Comey's Dictionary of Chemical Solubilities. If the funds will permit, add to the list Watt's Dictionary of Chemistry, which in itself is an almost inexhaustible source of information.

Finally, neither laboratory facilities, libraries, nor able instructors can insure a thoroughly reliable and well-disciplined chemist. The same virtues and qualities that make for success in other lines of work are no less necessary and efficient in the chemical laboratory. Patience, determination, energy, courage, good judgment, and absolute integrity are inseparable from the highest order of effort, and in proportion as they are lacking the results will be unsatisfactory and disappointing. Downright hard work is more than genius, and perseverance more than opportunity.

PART I.—METALS.

PART I.

DETERMINATION AND SEPARATION OF THE MORE COMMONLY OCCURRING METALS.

GROUP I.

LEAD, SILVER, MERCURY.

Experiment 1. — Lead.

(*a*) Measure out a small quantity (5 cc.) solution of lead nitrate, $Pb(NO_3)_2$, in a graduated test-tube. Add hydrochloric acid, HCl, a few drops at a time, as long as precipitation continues. What salt is formed?

(*b*) Filter and wash the precipitate with a little cold water.

(*c*) Pierce the bottom of the filter with a glass rod, and wash the precipitate through into a clean test-tube.

(*d*) Boil the precipitate in water. Does it dissolve? Filter and test the filtrate by adding a few drops of potassium chromate, K_2CrO_4. Chrome yellow, $PbCrO_4$, will be precipitated. *This is a test for Lead.*

SUPPLEMENTARY. — 1. To 5 cc. solution of lead nitrate, $Pb(NO_3)_2$, add a few drops of sulphuric acid, H_2SO_4. Result? Try to dissolve the precipitate in caustic soda, $NaOH$. Result?

2. To 5 cc. solution of lead nitrate add a few drops of solution of potassium iodide, KI. The precipitate is lead iodide, PbI_2. Describe it. Dissolve in boiling water. Allow the solution to cool, and note the golden crystalline scales deposited.

3. Into 5 cc. solution of lead nitrate pass a small quantity of hydro*gen sulphide, H_2S.* Result?

4. To 5 cc. solution of lead nitrate add 1 cc. or 2 cc. of ammonium hydroxide, NH_4OH. Result? Try to dissolve the precipitate in caustic soda. Result?

Notes and Suggestions.

1. If only a portion of the precipitate dissolves in (*d*), do not conclude that the residue is insoluble. Try adding more water.

Experiment 2. — Silver.

(*a*) Repeat Experiment 1, using silver nitrate, $AgNO_3$, instead of lead nitrate, $Pb(NO_3)_2$, proceeding as far as (*d*). Boil the precipitate. Is silver chloride, AgCl, soluble in hot water?

(*b*) Filter and pour ammonium hydroxide, NH_4OH, over the precipitate on the filter paper. The precipitate should dissolve.

(*c*) Test the filtrate by acidulating with dilute nitric acid, HNO_3. The equation is: $(NH_3)_3(AgCl)_2 + 3\,HNO_3 = 2\,AgCl + 3\,NH_4NO_3$. The *Silver* is reprecipitated as a chloride as soon as the alkaline solvent, ammonium hydroxide, is neutralized. *This confirms the presence of Silver.*

SUPPLEMENTARY. — 1. To 5 cc. solution of silver nitrate add a small quantity of solution of potassium chromate, K_2CrO_4. Result? Try to dissolve the precipitate in hot nitric acid, HNO_3. Result?

2. Into 5 cc. solution of silver nitrate pass hydrogen sulphide, H_2S. Result? Try to dissolve the precipitate in boiling nitric acid.

3. To 5 cc. solution of silver nitrate add a few drops of ammonium hydroxide, NH_4OH. Result? Continue adding ammonium hydroxide and stirring until the precipitate redissolves.

Notes and Suggestions.

1. In dissolving the precipitate off the filter in (*b*), pour the same portion of the solvent repeatedly over the paper in order to secure a saturated or nearly saturated solution.

2. Before adding the nitric acid in (*c*) it is an advantage to boil the solution several minutes in order to expel the greater part of the ammonia. In fact, this is quite necessary when only traces of silver salts are present, because of the solubility of silver chloride in ammonium salts.

Scheme 1. — Lead and Silver.

Devise and state a scheme for the separation and determination of *Lead* and *Silver* in solution of their salts.

Experiment 3. — Lead and Silver.

(*a*) Take 5 cc. solution containing both lead nitrate and silver nitrate. Separate and confirm the presence of *Lead* and *Silver* according to Scheme 1.

Experiment 4. — Mercury(ous).

(*a*) Repeat Experiment 1, using solution of mercurous nitrate, $HgNO_3$, instead of lead nitrate, proceeding as far as (*d*).

(*b*) Boil the precipitate in water. Does it dissolve? What other chloride does it resemble in this respect?

(*c*) Filter and try to dissolve the precipitate in ammonium hydroxide, NH_4OH, as in Experiment 2, (*b*). Does it dissolve? What effect has the ammonium hydroxide on the color of the precipitate? *This coloring of the chloride by the ammonium hydroxide is a characteristic test for Mercury(ous).*

SUPPLEMENTARY. — 1. To 5 cc. solution of mercurous nitrate add solution of stannous chloride, $SnCl_2$. A white or gray precipitate of mercurous chloride, $HgCl$, often mixed with gray metallic mercury, is precipitated.

2. Into 5 cc. solution of mercurous nitrate pass hydrogen sulphide, H_2S. Mercuric sulphide, HgS, mixed with metallic mercury, is precipitated. Try to dissolve it in boiling nitric acid, HNO_3. Result?

3. To 5 cc. solution of mercurous nitrate add a small quantity of potassium chromate, K_2CrO_4. Mercurous chromate, Hg_2CrO_4, is precipitated.

4. To 5 cc. solution of mercurous nitrate add 1 or 2 cc. of ammonium hydroxide. Result? Try to dissolve the precipitate in excess of ammonium hydroxide. This black insoluble precipitate is a mixture of mercury and mercur-ammonium nitrate, $Hg + (NH_2HgNO_3)HgO$.

5. Into 5 cc. solution of mercurous nitrate introduce a strip of *bright* copper foil. Remove after a few minutes and rub dry. Result?

Scheme 2. — Mercury(ous) and Silver.

Devise and state a scheme for the separation and determination of *Silver* and *Mercury*(*ous*) in solution of their salts.

Scheme 3. — Mercury(ous) and Lead.

Devise and state a scheme for the separation and determination of *Lead* and *Mercury*(*ous*) in solution of their salts.

Experiment 5. — Lead, Silver, and Mercury(ous).

(*a*) Take 5 cc. solution containing all three salts, lead nitrate, silver nitrate, and mercurous nitrate. Add dilute hydrochloric acid, HCl, little by little, as long as precipitation continues. Filter. Wash the precipitate with cold water and throw away the filtrate.

(*b*) Pierce the filter paper and wash the precipitate through into a clean test-tube. Boil. Filter. Test the filtrate with a few drops of potassium chromate, K_2CrO_4. Which salt is dissolved by the hot water? What is precipitated by the potassium chromate? Write the equation for the last reaction.

(*c*) To the residue on the filter paper add ammonium hydroxide, NH_4OH, pouring the filtrate back upon the filter

paper two or three times. Which salt is dissolved? Test the filtrate as in Experiment 2, (*c*).

(*d*) Which salt is blackened upon the filter paper? The formula of this black product being $Hg + NH_2HgCl$, write the equation.

Notes and Suggestions.

1. A large excess of hydrochloric acid should be avoided, as both silver chloride and mercurous chloride are somewhat soluble in this reagent.

2. If the lead chloride is not completely removed in (*b*), it will be changed by ammonium hydroxide to white insoluble $Pb_2OCl_2 \cdot H_2O$, some of which will appear in the filtrate in (*c*). It dissolves instantly, however, upon the addition of the dilute nitric acid.

3. If hydrochloric acid be added to a complex solution, consisting of the salts of *lead*, *silver*, *mercury*(*ous*), and any other metals, the only elements precipitated as insoluble chlorides are *lead*, *silver*, and *mercury*(*ous*). These three constitute a group, the first of several groups into which the metallic elements are divided for the purposes of chemical analysis.

4. The reagent by means of which a group reaction is exhibited is called the *general reagent* of the group.

Reactions in Group I.

Balance these equations: —

1. $PbO + HNO_3 = Pb(NO_3)_2 + H_2O$.
2. $Ag + HNO_3 = AgNO_3 + NO + H_2O$.
3. $Hg + HNO_3 = HgNO_3 + NO + H_2O$.
4. $Pb(NO_3)_2 + HCl = \underline{PbCl_2} + HNO_3$.
5. $AgNO_3 + HCl = \underline{AgCl} + HNO_3$.
6. $HgNO_3 + HCl = \underline{HgCl} + HNO_3$.
7. $PbCl_2 + H_2O =$ solution $PbCl_2$.

8. $PbCl_2 + K_2CrO_4 = \underline{PbCrO_4} + KCl.$
9. $AgCl + NH_3 = (NH_3)_3\,(AgCl)_2.$
10. $(NH_3)_3\,(AgCl)_2 + HNO_3 = AgCl + NH_4NO_3.$
11. $HgCl + NH_3 = \underline{Hg + NH_2HgCl} + NH_4Cl.$

The precipitates are underscored.

GROUP II.

ARSENIC, ANTIMONY, TIN, MERCURY(IC), LEAD, BISMUTH, COPPER, AND CADMIUM.

General Remarks. — The second group of metals includes those which form soluble chlorides, but which are precipitated as sulphides in dilute acid solution by hydrogen sulphide. Lead is classed in this group because it is not completely precipitated in the first group by hydrochloric acid, but is precipitated by hydrogen sulphide.

The use of hydrogen sulphide for the purpose of isolating the metals of the second group presupposes the previous acidulation of the solution with hydrochloric acid, even if no member of the first group be present in the mixture to be analyzed.

Experiment 6. — Arsenic.

(*a*) To 5 cc. solution of sodium arsenite, Na_3AsO_3, add just sufficient hydrochloric acid, HCl, to react quickly with litmus. Is there any precipitate? Heat until quite hot, and pass in hydrogen sulphide, H_2S, until precipitation is complete. Filter. Wash the precipitate thoroughly with cold water and throw away the filtrate.

(*b*) Pierce the filter with a glass rod and wash the precipitate into a small evaporating dish.

(*c*) Add yellow ammonium sulphide, $(NH_4)_2S_x$, using no more than necessary, stirring for some time, and heating *gently.* *The* precipitate should dissolve.

NOTE. — $(NH_4)_2S_x$ may be prepared by *gently* warming in a test-tube a little $(NH_4)_2S$, ammonium sulphide, with a pinch of flowers of sulphur.

Experiment 7. — Antimony.

Repeat Experiment 6, using solution of tartar emetic, $KSbO(C_4H_4O_6)$, instead of sodium arsenite, Na_3AsO_3. Does the precipitate dissolve at point (*c*)?

NOTE. — When hydrochloric acid, HCl, is added to a solution of an *antimony* salt, a precipitate, the oxychloride, $Sb_4O_5Cl_2$, is often thrown down, but dissolves in excess of the reagent. No more hydrochloric acid should be used for the purpose of redissolving the precipitate than is absolutely necessary.

Experiment 8. — Tin, Copper, Bismuth, Mercury, Lead, Cadmium.

(*a*) Repeat Experiment 6, using stannous chloride, $SnCl_2$, copper nitrate, $Cu(NO_3)_2$, bismuth nitrate, $Bi(NO_3)_3$, mercuric nitrate, $Hg(NO_3)_2$, lead nitrate, $Pb(NO_3)_2$, and cadmium nitrate, $Cd(NO_3)_2$, successively, and determine whether their sulphides are soluble in $(NH_4)_2S_x$, yellow ammonium sulphide.

(*b*) Separate the metals of the second group into two divisions based on the solubility of their sulphides in yellow ammonium sulphide, classing the soluble ones in division A and the insoluble in division B.

Notes and Suggestions.

1. The necessity of avoiding a large excess of hydrochloric acid in all these experiments cannot be too strongly emphasized, as it interferes with the formation of many precipitates.
2. In the case of bismuth, the oxychloride, BiOCl, is often precipitated upon the addition of hydrochloric acid, but dissolves in excess.

3. Since the *lead* will be largely precipitated by hydrochloric acid, the lead chloride, $PbCl_2$, should be filtered out, and hydrogen sulphide passed into the filtrate only.

4. It is a safe practice, after precipitating with hydrogen sulphide and filtering, to dilute the filtrate with two or three times its volume of water, and add more hydrogen sulphide.

Experiment 9. — Arsenic.

(*a*) Take 5 cc. solution of sodium arsenite, Na_3AsO_3. Acidulate with dilute hydrochloric acid. Heat almost to boiling, and pass hydrogen sulphide gas to saturation. Note the color of the precipitate. Warm for some time, adding more hydrogen sulphide, if necessary, until the solution smells strongly of it after shaking. Filter and wash thoroughly with water containing a little hydrogen sulphide. Remove the precipitate to an evaporating dish. Add a small quantity of yellow ammonium sulphide, and digest warm for about fifteen minutes. The arsenious sulphide, As_2S_3, should dissolve. Acidulate with hydrochloric acid which has been diluted with an equal volume of hydrogen sulphide solution. Arsen*ic* sulphide is precipitated. Filter and wash with hot water until free from hydrochloric acid. Remove to an evaporating dish and digest with a saturated solution of ammonium carbonate, $(NH_4)_2CO_3$.

(*b*) The arsen*ic* sulphide should dissolve. Acidulate with hydrochloric acid. Arsen*ic* sulphide is again precipitated. Filter and *wash*. Dry the residue on the filter slowly and carefully at 100° C.

(*c*) Introduce a small portion into an ignition tube closed at one end, and carefully put over it about six times its bulk of a mixture of equal parts of *dry* sodium carbonate, Na_2CO_3, and potassium cyanide, KCN.

(*d*) Heat the tube above the mixture and then the mix*ture itself gently*. Wipe out any moisture in the upper

part of the tube with a twisted piece of tissue paper. Heat the sealed end and contents to cherry red. Arsenic is sublimed and deposited as a black or brownish ring in the cool upper part of the tube. *This is a test for Arsenic.*

SUPPLEMENTARY. — 1. To 5 cc. solution of sodium arsenite, Na_3AsO_3, add sufficient hydrochloric acid to acidify. Put into the solution a strip of bright copper wire or foil. A gray film of copper arsenide will be deposited on the copper, which may be dried by filter paper, and heated in a dry test-tube to obtain a crystalline sublimate of arsenic trioxide, As_2O_3.

2. To 5 cc. solution of sodium arsenite add a small quantity of silver nitrate, $AgNO_3$. Silver arsenite, Ag_3AsO_3, is precipitated. Try to dissolve the precipitate in ammonium hydroxide. Result ?

3. Repeat 2, using copper sulphate, $CuSO_4$, instead of silver nitrate. The precipitate is copper arsenite, $CuHAsO_3$.

4. Into 5 cc. solution of sodium arsenite pass hydrogen sulphide, H_2S. Is there any precipitate ? Now acidulate with hydrochloric acid, HCl. Explain.

5. To 5 cc. solution of sodium arsenite add a small quantity of ammonium sulphide, $(NH_4)_2S$. Result? Acidulate with hydrochloric acid. The precipitate is arsenious sulphide. Explain.

6. Repeat Experiment 9, proceeding as far as (*c*). Dissolve the arsenic sulphide in aqua regia, evaporate off the excess of acid, and dilute with water. Add a nitric acid solution of ammonium molybdate, $(NH_4)_2MoO_4$, in considerable excess, and heat. A yellow precipitate of ammonium arseno-molybdate, $(MoO_3)_{12}(NH_4)_3AsO_4$, proves the presence of arsenic.

Notes and Suggestions.

1. No more hydrochloric acid should be used for the reprecipitation of the arsenic sulphide than is absolutely necessary.

2. More or less free sulphur is likely to be thrown down with the arsen*ic* sulphide, but may usually be disregarded. Since the sulphur is white, it may appreciably lighten the color of the whole precipitate. In case there is reason to suspect that it is present in any considerable proportion, it can be gotten rid of by shaking the precipitate with a small quantity of benzol and decanting. If all the precipitate should *dissolve, it is* evident that it was merely separated sulphur.

3. The object of this experiment, as of most experiments, is not simply to make a test for the particular substance under examination, but to study its most important reactions, especially those that are of value in analytical operations. The relation of these reactions to the schemes of separation will become apparent as the study of the second group progresses.

4. When arsenious sulphide dissolves in yellow ammonium sulphide, a sulpho-salt is formed: $As_2S_3 + 3(NH_4)_2S_x = 2(NH_4)_3AsS_4 + (3x-5)S$. When hydrochloric acid is added to this compound, a higher sulphide, As_2S_5, is precipitated: $2(NH_4)_3AsS_4 + 6HCl = 6NH_4Cl + 3H_2S + As_2S_5$.

5. From strongly acid arsen*ic* solutions, especially when heated, hydrogen sulphide precipitates arsen*ic* sulphide, As_2S_5. This form is likewise soluble in yellow ammonium sulphide.

Experiment 10. — Antimony.

(*a*) Repeat Experiment 9, using tartar emetic, $KSbO(C_4H_4O_6)$, instead of sodium arsenite, Na_3AsO_3, proceeding as far as (*b*). Does antimonic sulphide, Sb_2S_5, dissolve in ammonium carbonate, $(NH_4)_2CO_3$?

(*b*) Filter. Wash thoroughly. Free the precipitate from water as completely as possible. Remove the precipitate from the filter, and dissolve in the least necessary quantity of concentrated hydrochloric acid, adding a crystal of potassium chlorate to hasten solution.

(*c*) Heat gently to expel hydrogen sulphide or the excess of chlorine.

(*d*) Put the solution into an evaporating dish. Dilute with an equal quantity of water. Introduce a small piece of zinc, and bring the edge of a strip of platinum foil in contact with the zinc for a minute or two. The portion of the platinum immersed in the solution will be stained black by a thin deposit of *Antimony*. *This is a test for Antimony.*

SUPPLEMENTARY. — 1. To 5 cc. solution of tartar emetic add solution of caustic potash, KOH. Antimony trioxide, Sb_2O_3, is precipitated, *soluble in excess* of the reagent.

2. To 5 cc. solution of tartar emetic add ammonium hydroxide. Antimony trioxide, Sb_2O_3, is precipitated, insoluble in excess of the reagent.

3. Into 5 cc. solution of tartar emetic pass hydrogen sulphide. Result? Acidulate with hydrochloric acid. Explain.

4. Acidulate 5 cc. solution of tartar emetic with hydrochloric acid, and add ammonium sulphide, $(NH_4)_2S$. Result?

Notes and Suggestions.

1. Read Note 4, Experiment 8.

2. The test for *antimony* may be confirmed by dissolving the metallic deposit off the platinum with a few drops of hot nitric acid, HNO_3, to which a little tartaric acid has been added, diluting with water, and passing hydrogen sulphide into the solution. Orange colored antimonious sulphide, Sb_2S_3, will be precipitated.

3. While the precipitate first thrown down in (*a*) is antimoni*ous* sulphide, Sb_2S_3, the reprecipitated form is antimon*ic* sulphide, Sb_2S_5.

Scheme 4. — Arsenic and Antimony.

Devise and state a scheme for the separation and determination of *Arsenic* and *Antimony* in solution of their salts.

Experiment 11. — Arsenic and Antimony.

Take 5 cc. solution containing both tartar emetic, $KSbO(C_4H_4O_6)$, and sodium arsenite, Na_3AsO_3. Separate and make confirmatory tests for *Arsenic* and *Antimony* as per Scheme 4.

Experiment 12. — Tin.

(*a*) Repeat Experiment 10, using solution of stannous chloride, $SnCl_2$, instead of tartar emetic, $KSbO(C_4H_4O_6)$, proceeding as far as (*b*). Does stannic sulphide, SnS_2,

dissolve in ammonium carbonate, $(NH_4)_2CO_3$? Proceed to (*c*). Stannic sulphide, SnS_2, should dissolve in concentrated hydrochloric acid, HCl. Proceed to (*d*).

(*b*) Put the solution into an evaporating dish. Dilute with an equal quantity of water.

(*c*) Introduce two or three small pieces of zinc, and wait until action ceases, being sure that the zinc is in excess. Rinse and remove any undissolved pieces of zinc, and carefully wash by decantation the deposited crystalline scales or spongy particles of metallic *Tin*. Warm the residue with the least necessary quantity of concentrated hydrochloric acid. The *Tin* dissolves, forming stannous chloride. Transfer to a test-tube.

(*d*) Add to the solution a few drops of mercuric chloride, $HgCl_2$. A white or gray precipitate of mercurous chloride, HgCl, often mixed with gray or black metallic mercury, will be thrown down, for $2\ HgCl_2 + SnCl_2 = 2\ HgCl + SnCl_4$; and $2\ HgCl + SnCl_2 = 2\ Hg + SnCl_4$.

This is a test for Tin. Prove that the precipitate is mercurous chloride, HgCl, by applying the test under Experiment 4 (*c*).

SUPPLEMENTARY.—1. To 5 cc. solution of stannous chloride, $SnCl_2$, add a small quantity of caustic potash. Stannous hydroxide, $Sn(OH)_2$, is precipitated, soluble in excess of the reagent.

2. To 5 cc. solution of stannic chloride, $SnCl_4$, add a small quantity of caustic potash. Stannic acid, $SnO(OH)_2$, is precipitated, soluble in excess of the reagent.

3. Into 5 cc. solution of stannic chloride, $SnCl_4$, pass hydrogen sulphide. Stannic sulphide, SnS_2, is precipitated.

4. To 5 cc. solution of stannous chloride, $SnCl_2$, add a small quantity of ammonium hydroxide. Result? Try to dissolve the precipitate of stannous hydroxide, $Sn(OH)_2$, in excess of ammonium hydroxide. Result?

5. To 5 cc. stannic chloride, $SnCl_4$, add a few drops of mercuric *chloride*, $HgCl_2$. Result?

6. Into 5 cc. solution of stannic chloride introduce a small nail or other piece of iron, and warm for some time. Decant into another vessel, and add a few drops of mercuric chloride, $HgCl_2$. Result? Explain.

7. To 5 cc. solution of stannous chloride, $SnCl_2$, add a small quantity of ammonium sulphide, $(NH_4)_2S$. Result?

Notes and Suggestions.

1. The formation of a white precipitate in (*d*) is not in itself conclusive evidence of the presence of *tin*. Lead is likely to be present as an impurity in the zinc, some of it dissolving in the strong hydrochloric acid, and precipitating as a chloride when the solution is diluted with the mercuric chloride.

2. The precipitate first thrown down in (*a*) is stann*ous* sulphide, SnS, but the reprecipitated form is stann*ic* sulphide, SnS_2.

Scheme 5. — Arsenic and Tin.

Devise and state a scheme for the separation and determination of *Arsenic* and *Tin* in solution of their salts.

Scheme 6. — Antimony and Tin.

Devise and state a scheme for the separation and determination of *Antimony* and *Tin* in solution of their salts.

Notes and Suggestions.

1. Both metals are deposited in the metallic condition through the action of the zinc-platinum couple, the *antimony* chiefly as a black stain upon the platinum foil, the *tin* in part as black spongy particles, and in part as a white coating upon the platinum. The deposited *tin* is soluble in concentrated hydrochloric acid, while the *antimony* is insoluble.

Scheme 7. — Arsenic, Antimony, and Tin.

Devise and state a scheme for the separation and determination of *Arsenic*, *Antimony*, and *Tin* in solution of *their salts.* [For the modified Marsh method, see App.]

Experiment 13. — Arsenic, Antimony, and Tin.

Take 5 cc. solution containing tartar emetic, $KSbO(C_4H_4O_6)$, sodium arsenite, Na_3AsO_3, and stannous chloride, $SnCl_2$. Separate and make confirmatory tests for *Arsenic*, *Antimony*, and *Tin*, as per Scheme 7.

Notes and Suggestions.

1. Much care should be exercised in acidulating the solution in the first step of the experiment. An insufficient quantity of hydrochloric acid will mean a loss of arsenic, while if too strongly acid the antimony will be incompletely precipitated. The safest plan is to make the solution rather strongly acid in the beginning, and then, after passing hydrogen sulphide and filtering, to cool the filtrate, dilute with two or three times its volume of water, and again add hydrogen sulphide.

2. A large precipitate is not necessarily a sufficient one. Unless otherwise directed, add a reagent until precipitation is complete.

3. The ammonium carbonate, $(NH_4)_2CO_3$, used for the purpose of isolating the arsenic sulphide, should be as free as possible from ammonia in order to avoid loss of stannic sulphide and antimonic sulphide.

Experiment 14. — Mercury(ic).

(*a*) Take 5 cc. solution of mercuric nitrate, $Hg(NO_3)_2$. Add a few drops of dilute hydrochloric acid. Pass in hydrogen sulphide gas until no further precipitate is formed. Filter. Wash the precipitate thoroughly with water until the filtrate is free from acid when tested with litmus paper. Put the precipitate into an evaporating dish. Put over it four or five times as much dilute nitric acid, HNO_3, as is sufficient to cover it. Boil eight or ten minutes, stirring constantly, and replacing the water lost by evaporation.

(*b*) The mercuric sulphide, HgS, does not dissolve. This indicates a mercuric salt. To confirm the presence of *Mercury*(*ic*), evaporate to one-half the original volume.

Then add about 5 cc. concentrated hydrochloric acid and a crystal of potassium chlorate, and boil until the mercuric sulphide dissolves. Heat until chlorine ceases to pass away. Dilute with water. Add a few drops of stannous chloride, $SnCl_2$. A white or gray precipitate of mercurous chloride, $HgCl$, often mixed with metallic *Mercury*, is formed. *This is a test for Mercury(ic).*

SUPPLEMENTARY. — 1. To 5 cc. solution of mercuric nitrate add a few drops of caustic potash. The yellow precipitate is mercuric oxide, HgO, insoluble in excess of the reagent.

2. To 5 cc. solution of mercuric nitrate add a few drops of potassium chromate, K_2CrO_4. The precipitate is mercuric chromate, $HgCrO_4$.

3. To 5 cc. solution of mercuric nitrate add a small quantity of ammonium hydroxide. Dimercur-ammonium nitrate, $(NH_2HgNO_3)_2HgO$, is precipitated.

4. Into 5 cc. acidulated solution of mercuric nitrate introduce a strip of copper foil. Remove after a few minutes and rub dry. Result?

5. To 5 cc. solution of mercuric nitrate add a small quantity of ammonium sulphide, $(NH_4)_2S$. Result?

Notes and Suggestions.

1. If the heating of the mercuric sulphide in nitric acid is prolonged, or if the acid becomes concentrated, the mercuric sulphide is likely to be converted into a white compound, $Hg(NO_3)_2(HgS)$.

2. The peculiar and progressive variation of color from white to black, produced when hydrogen sulphide is passed into the mercuric nitrate, is characteristic of mercuric salts. Sufficient hydrogen sulphide should be added to insure complete transformation into the black sulphide.

Experiment 15. — Lead.

(*a*) Repeat Experiment 14, using solution of lead nitrate, $Pb(NO_3)_2$, instead of mercuric nitrate, $Hg(NO_3)_2$, proceeding as far as (*b*). The precipitate should dissolve.

(*b*) To the solution add 3 cc. concentrated sulphuric acid, and evaporate on a sand-bath or an iron plate until

sulphuric acid fumes begin to appear. Cool, add 25 cc. water, and pour into a beaker.

(*c*) Lead sulphate, $PbSO_4$, will be thrown down as a white powder, and may be made to collect in the centre by giving the beaker a rotary motion.

(*d*) To confirm the presence of *Lead*, filter and wash until the filtrate is no longer acid to litmus. Dissolve in a small quantity of ammonium acetate, and add a few drops of potassium chromate, K_2CrO_4. A yellow precipitate of lead chromate, $PbCrO_4$ (chrome yellow), is formed. *This is a test for Lead.*

(*e*) Upon what fact does the separation of *Mercury* and *Lead* in the second group depend?

Notes and Suggestions.

1. Hydrogen sulphide fails to precipitate lead salts in the presence of a considerable excess of mineral acids, unless largely diluted or partly neutralized.

2. If much hydrochloric acid is present, hydrogen sulphide is likely to produce a red precipitate, gradually changing to black.

3. To insure success in this experiment, the nitric acid used for the purpose of dissolving the lead sulphide, PbS, should be moderately dilute (15 to 25 per cent), and should not be allowed to become concentrated until all the lead sulphide has dissolved. A stronger acid is liable to change some or all of the lead sulphide into white insoluble lead sulphate, $PbSO_4$. The little masses of sulphur frequently formed through the action of nitric acid on sulphides should not be mistaken for undissolved lead sulphide.

Experiment 16. — Bismuth.

(*a*) Repeat Experiment 15, using solution of bismuth nitrate, $Bi(NO_3)_3$, instead of lead nitrate, $Pb(NO_3)_2$, proceeding to (*c*). Is any precipitate produced upon adding *sulphuric acid?*

(*b*) Add ammonium hydroxide to the solution in repeated small quantities until the solution is alkaline, stirring constantly, and heating to boiling.

(*c*) A white precipitate of bismuth hydroxide, $Bi(OH)_3$, results. To confirm the presence of *Bismuth*, filter, allow to drain a few minutes, and dissolve in the least necessary quantity of concentrated hydrochloric acid, adding a drop at a time until the precipitate is dissolved. Excess of hydrochloric acid must positively be avoided. Carefully evaporate the acid solution to a bulk of three or four drops, and pour it into a beaker nearly full of water. A milky turbidity, caused by precipitation of insoluble basic chloride of bismuth, $BiOCl$, *confirms the presence of Bismuth.*

(*d*) Upon what fact does the separation of *Bismuth* and *Mercury*(*ic*) depend? *Bismuth* and *Lead?*

SUPPLEMENTARY. — 1. Pour a few drops of bismuth nitrate solution into a test-tube of water. Bismuth nitrate reacts with water and forms insoluble basic bismuth nitrate, $BiONO_3$.

2. To 5 cc. solution of bismuth nitrate add a few drops of potassium chromate, K_2CrO_4. Yellow bismuth chromate, $Bi_2(CrO_4)_3$, is precipitated. It differs from lead chromate in being easily soluble in dilute nitric acid and insoluble in caustic potash.

3. To 5 cc. solution of bismuth nitrate add a small quantity of ammonium sulphide, $(NH_4)_2S$. Result?

4. Repeat Experiment 16, proceeding to (*c*). Filter, wash thoroughly, and treat the precipitate on the filter with a hot solution of potassium stannite, K_2SnO_2. A black precipitate proves the presence of *bismuth.*

Notes and Suggestions.

1. In solutions containing a considerable excess of hydrochloric or nitric acid the bismuth sulphide, Bi_2S_3, may fail to precipitate until after dilution with water.

2. The most striking characteristic of the normal bismuth salts is their ready decomposition by water and the consequent precipitation of insoluble basic salts. This reaction is the most noticeable in the

case of bismuth tri-chloride, $BiCl_3$, which is converted into the oxychloride, $BiOCl$, a form that is almost absolutely insoluble in water.

Experiment 17. — Copper.

(*a*) Repeat Experiment 16, using solution of copper nitrate, $Cu(NO_3)_2$, instead of bismuth nitrate, $Bi(NO_3)_3$, proceeding to (*c*). Is there any precipitate? The blue color imparted to the solution indicates the presence of *Copper*, and when *well defined is sufficient proof.*

(*b*) When testing for minute traces of *Copper*, the ammoniacal solution should be evaporated nearly to dryness, and acidulated with acetic acid. Then put it into a test-tube and add one or two drops of potassium ferrocyanide solution, $K_4Fe(CN)_6$. A reddish-brown precipitate or a light brownish-red turbidity *proves the presence of Copper.*

(*c*) Upon what fact does the separation of *Copper* and *Mercury*(*ic*) depend? *Copper* and *Lead?* *Copper* and *Bismuth?*

SUPPLEMENTARY. — 1. To 5 cc. solution of copper nitrate add a small quantity of caustic potash. The precipitate is copper hydroxide, $Cu(OH)_2$. Add caustic potash in excess, and then boil the mixture. The hydroxide changes to copper oxide, CuO.

2. To 5 cc. solution of copper nitrate add a few drops of hydrochloric acid and then put into it a bright piece of iron. Metallic copper will be deposited.

3. To 5 cc. solution of copper nitrate add a small quantity of ammonium sulphide. Copper sulphide, CuS, is precipitated. Try to dissolve it in solution of potassium cyanide, KCN. Result?

4. Dip the loop of a platinum wire into a solution of copper nitrate, and then introduce it into the Bunsen flame. Note the green color imparted to the flame.

Notes and Suggestions.

1. Ammonium hydroxide, added in small quantities, produces a greenish-blue precipitate of a basic salt, which is readily soluble in *excess of the reagent* to an azure-blue solution.

Experiment 18. — Cadmium.

(*a*) Repeat Experiment 16, using solution of cadmium nitrate, $Cd(NO_3)_2$, instead of bismuth nitrate, $Bi(NO_3)_3$, proceeding to (*c*). Is there any precipitate?

(*b*) Pass in hydrogen sulphide. A yellow precipitate of cadmium sulphide, CdS, *proves the presence of Cadmium.*

SUPPLEMENTARY. — 1. To 5 cc. solution of cadmium nitrate add a small quantity of caustic potash. Cadmium hydroxide, $Cd(OH)_2$, is precipitated, insoluble in excess of the reagent.

2. To 5 cc. solution of cadmium nitrate add a small quantity of ammonium sulphide, $(NH_4)_2S$. Cadmium sulphide, CdS, is precipitated. Try to dissolve it in solution of potassium cyanide, KCN. Result?

Notes and Suggestions.

1. If the solution is strongly acid, dilute with water before adding hydrogen sulphide.

2. Cadmium hydroxide, $Cd(OH)_2$, is thrown down by ammonium hydroxide, but redissolves in excess.

3. A yellow coloration upon the addition of hydrogen sulphide in (*b*) is not sufficient evidence of the presence of *cadmium*. There must be a yellow precipitate.

Experiment 19. — Copper and Cadmium.

(*a*) Repeat Experiment 16, using a mixture of cadmium nitrate, $Cd(NO_3)_2$, and copper nitrate, $Cu(NO_3)_2$, proceeding to (*c*).

(*b*) Divide the solution into two parts. Test one for *Copper*, as in Experiment 17 (*b*).

(*c*) To the other portion of the solution add potassium cyanide, KCN, solution, drop by drop, stirring constantly, until the solution is decolorized. Then test for *Cadmium as in* Experiment 18 (*b*).

(*d*) Upon what fact does the separation of *Cadmium* and *Mercury* depend? *Cadmium* and *Lead?* *Cadmium* and *Bismuth?*

Notes and Suggestions.

1. The separation of *copper* and *cadmium* depends upon the fact that copper sulphide is soluble in solution of potassium cyanide, forming the double colorless cyanide, KCN.CuCN, and that while *cadmium* forms a similar cyanide, it is decomposed by hydrogen sulphide, and the cadmium sulphide reprecipitated.

2. Potassium cyanide is one of the most dangerous poisons known, and should always be handled with the utmost caution. It should not be allowed to come into contact with abrasions of the skin, and should never be added to acid solutions, except under the hood, for fear of liberating the deadly hydrocyanic acid.

Scheme 8. — Mercury(ic), Lead, Bismuth, Copper, Cadmium.

Devise and state a scheme for the separation and determination of *Mercury(ic)*, *Lead*, *Bismuth*, *Copper*, and *Cadmium* in solution of their salts.

Experiment 20. — Mercury(ic), Lead, Bismuth, Copper, and Cadmium.

Take 5 cc. solution containing mercuric nitrate, $Hg(NO_3)_2$, lead nitrate, $Pb(NO_3)_2$, bismuth nitrate, $Bi(NO_3)_3$, copper nitrate, $Cu(NO_3)_2$, and cadmium nitrate, $Cd(NO_3)_2$. Separate and determine as per Scheme 8.

Notes and Suggestions.

1. Sufficient hydrogen sulphide should be added to insure complete precipitation of all members of the sub-group.

2. Hydrochloric acid must be thoroughly washed out before treatment with nitric acid, since otherwise the aqua regia formed will lead to *loss and complications.*

3. In case there is reason to suspect that any considerable proportion of the lead sulphide, PbS, has been oxidized to lead sulphate, $PbSO_4$, it is advisable to filter the residue of mercuric sulphide, HgS, and lead sulphate, $PbSO_4$, wash thoroughly, and boil with ammonium acetate. The lead sulphate will dissolve, and may be tested as in Experiment 15 (*d*). The residue of mercuric sulphide may then be dissolved and tested as in Experiment 14 (*b*).

4. The setting free of sulphur is incidental to the action of nitric acid on the sulphides of lead, bismuth, copper, and cadmium. It may be in the form of milk-white particles, so minute as to pass through the filter paper, or of tenacious yellow masses enclosing nuclei of lead sulphide, bismuth sulphide, and copper sulphide, and more or less obscuring the presence of mercuric sulphide.

5. If, in testing for *cadmium*, a black precipitate is obtained, due possibly to lead sulphide or mercuric sulphide, proceed as follows: Filter, wash, remove to a test-tube, and boil several minutes with an excess of dilute sulphuric acid (1 part acid to 4 parts water). Filter, and test the filtrate for *cadmium* with hydrogen sulphide.

Experiment 21. — Second Group.

(*a*) Take 10 cc. solution containing some unknown metals of the second group. Acidulate with dilute hydrochloric acid. Heat almost to boiling, and add hydrogen sulphide until no further precipitate is produced, as instructed in Experiment 9 (*a*). Filter, and wash the precipitate until the filtrate is no longer acid to litmus.

(*b*) Remove the precipitate to an evaporating dish. Add yellow ammonium sulphide, and digest for some time. The sulphides of division A dissolve; sulphides of division B do not. Filter and wash the precipitate once or twice with yellow ammonium sulphide and then with hot water; save the filtrate. Treat the residue on the filter as in Experiment 20, beginning at the point where dilute nitric acid is about to be added to the sulphides. To the filtrate *add dilute hydrochloric* acid until no further precipitate

forms. The sulphides of division A are reprecipitated. Filter and wash until no longer acid. Treat the residue as in Experiment 13, beginning at the point where ammonium carbonate is about to be added.

Notes and Suggestions.

1. To insure the success of this experiment, the student should review carefully the various "Notes and Suggestions" offered in connection with the several experiments of the second group.

2. Copper sulphide is somewhat soluble in yellow ammonium sulphide, and is reprecipitated by acids, sometimes as the normal sulphide, but frequently as the light-colored supersulphide. This latter form, when mixed with free sulphur, closely resembles the sulphides of *arsenic* and *tin*. The loss of copper sulphide is not likely to be sufficient to endanger the success of the *copper* determination.

3. Unless the lead has been completely removed with sulphuric acid it will be precipitated with the bismuth upon the addition of ammonium hydroxide.

4. In case the treatment with yellow ammonium sulphide has been insufficient, some of the *antimony* and *tin* will appear in Group B, to the confusion of the analyst. They are changed into oxides through the action of the nitric acid, and will be found mixed with the insoluble residue of mercuric sulphide.

Some Reactions in Group II.

Balance these equations: —

1. $SbCl_3 + H_2S = \underline{Sb_2S_3} + HCl.$
2. $Sb_2S_3 + (NH_4)_2S_x = (NH_4)_3SbS_4 + (3x - 5)S.$
3. $SnCl_2 + H_2S = \underline{SnS} + HCl.$
4. $Cu(NO_3)_2 + H_2S = \underline{CuS} + HNO_3.$
5. $Na_3AsO_3 + HCl + H_2S = \underline{As_2S_3} + NaCl + H_2O.$
6. $Bi(NO_3)_3 + H_2S = \underline{Bi_2S_3} + HNO_3.$
7. $Hg(NO_3)_2 + H_2S = \underline{HgS} + HNO_3.$
8. $Pb(NO_3)_2 + H_2S = \underline{PbS} + HNO_3.$

9. $Cd(NO_3)_2 + H_2S = \underline{CdS} + HNO_3$.

10. $Sb_2S_3 + HCl = SbCl_3 + H_2S$.

11. $SnS_2 + HCl = SnCl_4 + H_2S$.

12. $SnCl_4 + Zn = \underline{Sn} + ZnCl_2$.

13. $Sn + HCl = SnCl_2 + H$.

14. $CuS + HNO_3 = Cu(NO_3)_2 + S + NO + H_2O$.

15. $Cu(NO_3)_2 + NH_4OH = Cu(NH_3)_2O\,(NH_4NO_3)_2 + H_2$

16. $Bi(NO_3)_3 + NH_4OH = \underline{Bi(OH)_3} + NH_4NO_3$.

17. $Bi(OH)_3 + HCl = BiCl_3 + H_2O$.

18. $BiCl_3 + H_2O = \underline{BiOCl} + HCl$.

GROUP III.

IRON, ALUMINUM, CHROMIUM.

General Remarks. — This group includes those metals which are not precipitated in acid solution by hydrogen sulphide, and whose hydroxides are insoluble in the presence of ammonium salts. Ammonium hydroxide is the group reagent, in the presence of ammonium chloride.

Experiment 22. — Iron.

(*a*) Take 5 cc. solution of ferrous sulphate, $FeSO_4$. Add 1 cc. of hydrochloric acid. Is there any precipitate?

(*b*) Pass in a small quantity of hydrogen sulphide. Is there any precipitate?

(*c*) Boil until the odor of hydrogen sulphide is not perceptible. Add eight or ten drops of concentrated nitric acid, and boil three or four minutes to convert the *Iron* into the ferr*ic* condition. The color should change to pale yellow.

(*d*) Add a small quantity of solution of ammonium chloride, NH_4Cl (about one-half of the quantity of *Iron* solution), and then add ammonium hydroxide little by little, stirring constantly, until the odor of ammonia prevails. Boil one or two minutes longer.

(*e*) A brownish-red precipitate of ferric hydroxide, $Fe(OH)_3$, is formed. Filter. Wash thoroughly. Wash the precipitate into an evaporating dish. Add 2 or 3 cc.

of strong solution of caustic soda or caustic potash and boil several minutes. Does ferric hydroxide dissolve?

(*f*) Dilute with a considerable quantity of water, and filter. *Wash thoroughly.*

(*g*) Dissolve in a minimum quantity of concentrated hydrochloric acid, and dilute with twice its volume of water.

(*h*) Add slowly a few drops of potassium ferrocyanide, $K_4Fe(CN)_6$. The formation of Prussian blue, $Fe_4[Fe(CN)_6]_3$, *proves the presence of Iron.*

(*i*) Upon what fact does the separation of *Iron* from the first and second group metals depend?

SUPPLEMENTARY. — 1. To 5 cc. each of solutions of ferrous sulphate and ferric chloride, $FeCl_3$, in separate test-tubes, add a small quantity of ammonium hydroxide. The precipitates are ferrous and ferric hydroxides, respectively.

2. To 5 cc. each of solutions of ferrous sulphate and ferric chloride, in separate test-tubes, add a small quantity of solution of potassium ferricyanide, $K_3Fe(CN)_6$. In the former, Turnbull's blue, $Fe_3[Fe(CN)_6]_2$, is precipitated; in the latter, a green or brown coloration is produced.

3. Repeat 1, using caustic potash instead of ammonium hydroxide. The results are similar.

4. To 5 cc. each of solutions of ferrous sulphate, $FeSO_4$, and ferric sulphate, $Fe_2(SO_4)_3$, in separate test-tubes, add a little potassium thiocyanate, KCNS. In the former case there is no effect, but in the latter a blood-red coloration results, due to the formation of ferric thiocyanate, $Fe(CNS)_3$.

5. Into 5 cc. neutral solution of ferrous sulphate pass hydrogen sulphide. Black ferrous sulphide, FeS, is partially precipitated. Add dilute hydrochloric acid. Result?

6. Into 5 cc. ferric sulphate solution pass hydrogen sulphide. Sulphur is set free.

7. To 5 cc. each of ferrous sulphate and ferric sulphate in separate test-tubes add a little potassium ferrocyanide solution, $K_4Fe(CN)_6$. In the former a bluish-white precipitate of $K_2Fe_2(CN)_6$ is produced, *and in the latter* Prussian blue, $Fe_4[Fe(CN)_6]_3$.

8. To 5 cc. each of ferrous sulphate and ferric sulphate solutions in separate test-tubes add a small quantity of ammonium sulphide, $(NH_4)_2S$. Ferrous sulphide is precipitated, in the latter case mixed with free sulphur. Add a little dilute hydrochloric acid to each. The sulphides dissolve, but the liquid may be opaque from separated sulphur.

Notes and Suggestions.

1. Whatever the condition of the iron salt at the beginning of the experiment, it will be in the *ferrous* form after the introduction of the hydrogen sulphide. Since ferrous salts are incompletely precipitated by ammonium hydroxide, in the presence of ammonium chloride, it is necessary to convert them into the *ferric* state before continuing the analysis. The nitric acid is used for this purpose.

2. If an insufficient quantity of nitric acid is added in (*c*), the fact will be indicated by the formation of a green, slimy precipitate of ferrous hydroxide, $Fe(OH)_2$, upon the addition of the ammonium hydroxide. It should be redissolved in a little nitric acid and heated for a minute before precipitating anew with ammonium hydroxide.

3. The operation of washing the precipitated ferric hydroxide in (*e*) will be greatly facilitated by decantation.

4. The hydrogen sulphide must be completely expelled in (*c*), since its presence would lead to the formation of ammonium sulphide in (*d*) and consequent precipitation of the iron as a sulphide.

Experiment 23. — Aluminum.

(*a*) Repeat Experiment 22, using a solution of aluminum potassium sulphate, $AlK(SO_4)_2$, instead of ferrous sulphate $FeSO_4$, proceeding to (*f*). Does the aluminum hydroxide $Al(OH)_3$, dissolve?

(*b*) To the solution add sufficient hydrochloric acid barel to acidulate it. Then add ammonium hydroxide until alkaline, avoiding an excess, as the precipitate of aluminum hydroxide formed is slightly soluble in ammonium hydroxide. Warm gently, and set aside for at least thirt minutes. *A white gelatinous precipitate proves the presenc of Aluminum.*

(*c*) Upon what fact does the separation of *Aluminum* from the first and second groups depend?

(*d*) Upon what fact does the separation of *Iron* and *Aluminum* depend?

SUPPLEMENTARY.—1. To 5 cc. solution of aluminum chloride, $AlCl_3$, add a small quantity of ammonium sulphide, $(NH_4)_2S$. Aluminum hydroxide is thrown down as a white (often discolored) flocculent precipitate.

2. Heat a small quantity of solid aluminum potassium sulphate on charcoal in the blow-pipe flame, then moisten with cobalt nitrate, and heat again. An infusible blue mass is obtained.

3. To 5 cc. solution of aluminum potassium sulphate slowly add caustic potash solution. Aluminum hydroxide is precipitated, but redissolves in excess of the reagent, forming potassium aluminate, $KAlO_2$. Now add solution of ammonium chloride, and warm. Aluminum hydroxide is reprecipitated.

Notes and Suggestions.

1. The presence of ammonium chloride lessens the solubility of aluminum hydroxide in ammonium hydroxide.

2. It will be found advantageous in this experiment to wash the gelatinous precipitate of aluminum hydroxide by decantation.

Experiment 24.—Chromium.

(*a*) Repeat Experiment 22, using solution of potassium dichromate, $K_2Cr_2O_7$, instead of ferrous sulphate, $FeSO_4$, proceeding to (*g*), with this difference: A larger quantity of hydrochloric acid should be added to the solution, and hydrogen sulphide must be passed to saturation—*i.e.*, until the solution smells strongly of the reagent before heating; also, after adding ammonium hydroxide, it is necessary to boil a long time to insure the precipitation of chromium hydroxide, $Cr(OH)_3$.

(*b*) Fuse a portion of the residue with sodium carbonate, Na_2CO_3 (add a small quantity of potassium nitrate, KNO_3),

on platinum foil over the Bunsen flame. *A yellow mass,* consisting of sodium and potassium chromates, *indicates Chromium.* To confirm the presence of *Chromium,* dissolve the fused mass in water (filter if necessary), acidulate the filtrate with acetic acid, boil a few minutes to expel carbon dioxide, and add a few drops of lead acetate solution. A yellow precipitate of lead chromate, $PbCrO_4$, *proves the presence of Chromium.*

(*c*) Upon what fact does the separation of *Chromium* from the first and second groups depend?

(*d*) Upon what fact does the separation of *Chromium* and *Aluminum* depend?

SUPPLEMENTARY. — 1. To 5 cc. solution of chromium sulphate, $Cr_2(SO_4)_3$, add a small quantity of ammonium sulphide, $(NH_4)_2S$. Chromium hydroxide is formed as a bluish-green precipitate, insoluble in excess of the reagent.

2. Fuse some potassium chromate, K_2CrO_4, with borax in the reducing flame. A green bead is obtained.

3. To 5 cc. solution of chromium sulphate slowly add a small quantity of caustic potash solution. Chromium hydroxide is precipitated, but redissolves in excess of the reagent. Divide the solution into two parts. Boil one portion several minutes. Chromium hydroxide is reprecipitated. To the other add a small quantity of hot ammonium chloride. Chromium hydroxide is precipitated.

Notes and Suggestions.

1. *Chromium* will not be precipitated as a hydroxide unless present as a base in the solution. In potassium dichromate it plays the part of an acid radical. By adding hydrogen sulphide in the presence of hydrochloric acid, chromic chloride, $CrCl_3$, is formed as a greenish colored solution: $2\,K_2Cr_2O_7 + 16\,HCl + 6\,H_2S = 4\,CrCl_3 + 4\,KCl + 6\,S + 14\,H_2O$.

2. During the reduction of potassium dichromate to chromic chloride considerable sulphur is set free from the hydrogen sulphide, and being suspended in the green liquid might easily be mistaken for a green *precipitate.*

3. Chromium hydroxide is slightly soluble in excess of ammonium hydroxide in the cold, forming a pink solution, but is completely reprecipitated by boiling for some time; hence the precaution in (*a*).

4. The fact must not be overlooked that chromium hydroxide is soluble in excess of caustic potash in the cold, and that prolonged heating is required to reprecipitate it.

Experiment 25. — Iron, Aluminum, Chromium.

(*a*) Take 10 cc. solution containing ferrous sulphate, $FeSO_4$, aluminum potassium sulphate, $AlK(SO_4)_2$, and chromium sulphate, $Cr_2(SO_4)_3$. Repeat Experiment 24, proceeding to (*b*).

(*b*) Test the filtrate for *Aluminum* as in Experiment 23 (*b*).

(*c*) With a portion of the residue test for *Chromium* as in Experiment 24 (*b*).

(*d*) With the remainder test for *Iron* as in Experiment 22 (*g*) and (*h*).

SUPPLEMENTARY. — 1. Take 10 cc. solution containing ferrous sulphate, aluminum potassium sulphate, and chromium sulphate. Repeat Experiment 24, proceeding to (*b*). To the filtrate add ammonium chloride, warm, and let stand some time. A white flocculent precipitate proves the presence of aluminum. Wash the residue of ferric and chromium hydroxides through the filter with a little caustic soda or caustic potash, add a few cc. of hydrogen peroxide, H_2O_2, and heat. The chromium will be oxidized to the acid state. Filter, and test the filtrate for chromium by acidifying with acetic acid, and adding a few drops of lead acetate solution. Test the residue of ferric hydroxide for iron as in Experiment 22 (*g*) and (*h*).

Notes and Suggestions.

1. This method of determination of *iron*, *aluminum*, and *chromium* depends upon the fact that the presence of *chromium* in no wise interfere[illegible] with [illegible] sulp[illegible] for *iron*, and that while the fusion with sodium carb[illegible] chromium hydroxide into a soluble chromate, the ferr[illegible]ins unchanged and insoluble.

2. In case the separation of the chromium is incomplete, owing to insufficient boiling of the caustic potash solution, some of it may be thrown down with the aluminum, imparting a green color to the precipitate. In this event the precipitate should be filtered, dissolved in caustic potash, and the solution boiled for several minutes. Filter, and test the filtrate for aluminum as in Experiment 23 (*b*).

3. Before beginning this experiment the student should review very thoroughly all the instructions pertaining to the third group. He should consider especially the deportment of hydrochloric acid, hydrogen sulphide, nitric acid, ammonium hydroxide, ammonium chloride, and caustic potash toward the several members of the group, not forgetting that the reactions noted in the separate treatment of the salts will be somewhat obscured in the mixture.

4. Under the most favorable conditions there should be but little difficulty in the separation and determination of the third group metals, but in practical analysis the operations are liable to be seriously complicated through the presence of several extraneous substances. Among these are the phosphates of iron, aluminum, chromium, zinc, manganese, cobalt, nickel, barium, calcium, strontium, and magnesium, besides a number of oxalates, borates, silicates, fluorides, and aluminates. All these substances may be precipitated, wholly or in part, upon the addition of ammonium hydroxide, owing to the neutralization of the acid by which they were kept in solution. The method of procedure in such cases must be modified to suit the conditions, and is amply provided for in the scheme of analysis suggested on p. 120, but cannot be profitably studied at this point. The presence of fixed organic matter, such as albumin, starch, sugar, tartaric acid, etc., partially or completely prevents the precipitation of the third group, and in the regular course of analysis should be destroyed as directed on p. 124.

5. In order that the test for *aluminum* may be considered conclusive, the sodium or potassium hydroxide used for separating this metal from the other members of the group must be free from aluminum salts. If there is the least doubt as to the purity of the reagent, it is advised that the following plan of separation, known as Parr's method, be substituted for the procedure in Experiment 25: —

Take 10 cc. solution containing ferrous sulphate, aluminum potassium sulphate, and chromium sulphate. Repeat Experiment 22, proceeding to (*e*). Filter, wash thoroughly, and transfer to a test-tube. Add 10 or 15 cc. of water and a few small pieces of sodium peroxide,

Na_2O_2. Boil until effervescence ceases. Filter and wash. The r due on the filter paper is ferric hydroxide. Test it for *iron* as in Exp ment 22 (*g*) and (*h*). The filtrate contains sodium chromate, Na_2Cr and sodium aluminate, $NaAlO_2$. Divide it into two parts. Test for *aluminum* as in Experiment 23 (*b*). Acidulate the second port with acetic acid, and test for *chromium* by adding a few drops of l acetate solution, as in Experiment 24 (*b*). The equations repres ing the action of the sodium peroxide are as follows: —

$$2\,Cr(OH)_3 + 3\,Na_2O_2 = 2\,Na_2CrO_4 + 2\,H_2O + 2\,NaOH.$$

$$Al(OH)_3 + NaOH = NaAlO_2 + 2\,H_2O.$$

Some Reactions in Group III.

Balance these equations: —

1. $Fe + H_2SO_4 = FeSO_4 + H.$
2. $FeSO_4 + HNO_3 = Fe_2(SO_4)_3 + H_2O + NO + Fe(NO_3$
3. $Fe_2(SO_4)_3 + NH_4OH = \underline{Fe(OH)_3} + (NH_4)_2SO_4.$
4. $Fe(OH)_3 + HCl = FeCl_3 + H_2O.$
5. $FeCl_3 + K_4Fe(CN)_6 = Fe_4[Fe(CN)_6]_3 + KCl.$
6. $AlK(SO_4)_2 + NH_4OH = \underline{Al(OH)_3} + (NH_4)_2SO_4 + K_2SO_4.$
7. $Al(OH)_3 + NaOH = NaAlO_2 + H_2O.$
8. $NaAlO_2 + HCl = AlCl_3 + NaCl + H_2O.$
9. $K_2Cr_2O_7 + HCl + H_2S = CrCl_3 + KCl + H_2O + S.$
10. $Na_2CrO_4 + Pb(C_2H_3O_2)_2 = \underline{PbCrO_4} + Na(C_2H_3O_2).$

GROUP IV.

ZINC, MANGANESE, COBALT, NICKEL.

General Remarks. — This group includes those metals (except *Iron*) whose sulphides are insoluble in alkaline solutions but soluble in dilute hydrochloric acid. They are precipitated, therefore, by ammonium sulphide in neutral solutions and by hydrogen sulphide in alkaline solutions. Ammonium sulphide is the group reagent in the presence of ammonium hydroxide and ammonium chloride.

Experiment 26. — Zinc.

(*a*) Take 5 cc. solution of zinc nitrate, $Zn(NO_3)_2$. Add a few drops of hydrochloric acid. Is there any precipitate? Pass into it a small quantity of hydrogen sulphide. Is there any precipitate? Boil to expel the hydrogen sulphide. Add a few drops of concentrated nitric acid. Add ammonium chloride, NH_4Cl, and ammonium hydroxide, as in Experiment 22 (*d*). Is there any precipitate?

(*b*) Add ammonium sulphide, $(NH_4)_2S$, to the boiling solution, drop by drop, stirring constantly, as long as a precipitate forms.

(*c*) Zinc sulphide, ZnS, is precipitated. Warm the vessel containing the precipitate until the sulphide settles. Filter and wash with hot water containing a little ammonium sulphide, then once with water alone. Put into a test-tube. Add *cold* dilute hydrochloric acid, made by diluting 1 part of concentrated acid with 5 parts of water.

(*d*) The precipitate should dissolve. Boil to expel

hydrogen sulphide. *Cool.* Add strong caustic potash solution *in excess*, without boiling. [Zinc hydroxide, $Zn(OH)_2$, is precipitated, but redissolves in excess of caustic potash.]

(*e*) Acidulate with acetic acid, and add hydrogen sulphide. A white or nearly white flocculent precipitate of zinc sulphide, ZnS, *proves the presence of Zinc.*

SUPPLEMENTARY. — 1. Into 5 cc. of neutral solution of zinc nitrate pass hydrogen sulphide. White hydrated zinc sulphide, $ZnS \cdot H_2O$, is partially precipitated. Add hydrochloric acid. Result?

2. Moisten a small quantity of solid zinc nitrate with solution of cobalt nitrate, and heat on charcoal before the blow-pipe. A bright green infusible mass is obtained.

3. To 5 cc. solution of zinc nitrate add excess of caustic potash in the cold. Zinc hydroxide is precipitated, but redissolves in excess of the reagent, forming potassium zincate, K_2ZnO_2. Divide the solution into two parts. Dilute and boil one portion. Zinc hydroxide is reprecipitated. To the other add ammonium chloride. No effect is produced.

Notes and Suggestions.

1. The presence of hydrochloric acid is necessary in (*a*) to prevent the partial precipitation of zinc sulphide by hydrogen sulphide.

2. If a precipitate of zinc hydroxide should form in (*a*) upon the addition of ammonium hydroxide, add the reagent in excess, when the precipitate will redissolve.

3. While ammonium chloride helps to prevent the precipitation of zinc hydroxide in (*a*), it greatly promotes the separation of zinc sulphide in (*b*).

4. Frequently the precipitated zinc sulphide in (*e*) is discolored, or even decidedly dark, owing to traces of other sulphides. Iron, especially, during the course of separation is liable to be incompletely oxidized and precipitated in the third group, in which event it may appear at this point.

Experiment 27. — Manganese.

(*a*) Repeat Experiment 26, using solution of manganese nitrate, $Mn(NO_3)_2$, instead of zinc nitrate, $Zn(NO_3)_2$, proceeding to (*d*). Does manganese sulphide, MnS, dissolve?

Proceed to (*e*). Allow to stand some time and shake frequently. A white gelatinous precipitate of manganous hydroxide, $Mn(OH)_2$, forms, and rapidly turns brown, owing to the absorption of oxygen, forming $MnO(OH)$.

(*b*) Filter and wash thoroughly. Mix 5 cc. concentrated nitric acid with the same volume of water, add to the liquid about 1 gr. of *pure* lead peroxide, PbO_2. Warm to 50° or 60° in a test-tube, and stir in the precipitate from (*a*). A violet color appears as soon as the lead peroxide settles, and *proves the presence of Manganese.*

(*c*) Upon what fact does the separation of *Zinc* and *Manganese* from the first group metals depend? from the second group metals? from the third group metals?

(*d*) Upon what fact does the separation of *Zinc* and *Manganese* depend?

SUPPLEMENTARY. — 1. To 5 cc. solution of manganese nitrate add a small quantity of ammonium hydroxide. Manganous hydroxide is precipitated, insoluble in excess of the reagent. Now add ammonium chloride in successive small portions. The precipitate dissolves with difficulty.

2. Into 5 cc. neutral solution of manganese nitrate pass hydrogen sulphide. No precipitate is formed. Now add ammonium hydroxide to make alkaline. Hydrated manganous sulphide, $MnS.H_2O$, is thrown down as a flesh-colored precipitate.

Notes and Suggestions.

1. Whatever the condition of the manganese salt at the beginning of the experiment, it will be in the mangan*ous* form after the introduction of the hydrochloric acid and the hydrogen sulphide.

2. Manganous hydroxide, unlike zinc hydroxide, is insoluble in excess of ammonium hydroxide, but is soluble in ammonium chloride; hence, in the presence of the latter, ammonium hydroxide fails to produce a precipitate.

3. But a few drops of nitric acid should be added in (*a*), since there is danger of changing the mangan*ous* salt into the mangan*ic* form. In

this event, ammonium hydroxide will produce a precipitate of manganic hydroxide, MnO(OH), even in the presence of ammonium chloride.

4. In very dilute solutions ammonium sulphide produces a precipitate only after standing a long time in a warm place.

Experiment 28. — Cobalt.

(*a*) Repeat Experiment 26, using solution of cobalt nitrate, $Co(NO_3)_2$, instead of zinc nitrate, $Zn(NO_3)_2$, proceeding as far as (*d*). The cobalt sulphide, CoS, does not dissolve.

(*b*) Filter. Dissolve the black residue on the filter paper by the addition of a few drops of hot aqua regia. Evaporate the solution nearly to dryness. Add to the residual solution 50 cc. of nitrite of potassium solution, KNO_2, and then concentrated acetic acid, $HC_2H_3O_2$, until the reaction of the liquid is strongly acid. Transfer to a beaker, and leave in a moderately warm place for twenty-four hours.

(*c*) A crystalline precipitate of beautiful yellow color, consisting of the double nitrite of potassium and cobalt $[(KNO_2)_3\ Co(NO_2)_3 + Aq.]$, *indicates the presence of Cobalt.* Confirm the test by fusing a minute quantity of the precipitate with borax on a platinum wire in the blowpipe flame. The formation of a deep blue colored bead, consisting of sodium cobaltous metaborate, *proves the presence of Cobalt.*

(*d*) Upon what fact does the separation of *Cobalt* from the first group depend? from the second group? from the third group?

(*e*) Upon what fact does the separation of *Cobalt* and *Zinc* depend? *Cobalt* and *Manganese?*

SUPPLEMENTARY. — 1. Into 5 cc. neutral solution of cobalt nitrate *pass hydrogen* sulphide. No precipitate is formed except on long

standing, when cobalt sulphide is partially thrown down. Add ammonium hydroxide. Result?

2. Fuse a minute quantity of cobalt nitrate with borax on a platinum wire, in the blow-pipe flame. A deep blue bead is obtained.

3. To 5 cc. solution of cobalt nitrate add a little caustic potash. A blue precipitate of basic cobaltous salt is thrown down, insoluble in excess of the reagent, and turning green upon exposure to the air. Heat for a few minutes. The precipitate is converted into pale red cobaltous hydroxide, $Co(OH)_2$.

Notes and Suggestions.

1. The student is requested to make a careful review of Notes 1, 2, and 3 under the Zinc experiment, since the statements there made are equally true of *cobalt*.

2. After the precipitation of cobalt sulphide by ammonium sulphide, $(NH_4)_2S$, no more time than necessary should be spent in its examination and treatment, since the cobalt sulphide gradually oxidizes to the soluble sulphate.

3. Cobalt sulphide is soluble in hot concentrated hydrochloric acid, and slightly in cold, hence the effort in (*a*) to dissolve that salt should not be prolonged.

Experiment 29. — Nickel.

(*a*) Repeat Experiment 28, using solution of nickel nitrate, $Ni(NO_3)_2$, instead of cobalt nitrate, $Co(NO_3)_2$, proceeding as far as (*c*). Is any precipitate formed?

(*b*) Add a small quantity of caustic soda to the solution. An apple-green precipitate of nickel hydroxide, $Ni(OH)_2$, *indicates the presence of Nickel.* Confirm the test for *Nickel* by fusing a minute quantity of the precipitate with borax on a platinum wire in the oxidizing flame. A violet bead while hot, reddish brown when cold, *proves the presence of Nickel.*

(*c*) Upon what fact does the separation of *Nickel* from the first group depend? from the second group? from the third group?

(*d*) Upon what fact does the separation of *Nickel* and *Zinc* depend? *Nickel* and *Manganese?* *Nickel* and *Cobalt?*

SUPPLEMENTARY. — 1. To 5 cc. solution of nickel nitrate add a small quantity of solution of potassium cyanide. Nickel cyanide, $Ni(CN)_2$, is precipitated, but dissolves in excess of the reagent, forming potassium nickelous cyanide, $K_2Ni(CN)_4$. It is reprecipitated, however, upon adding a little hydrochloric or sulphuric acid.

2. Into 5 cc. neutral solution of nickel nitrate pass hydrogen sulphide. Only a slight precipitate of nickel sulphide, NiS, is formed. Add ammonium hydroxide, however, to make alkaline, and note the precipitation of the nickel sulphide.

Notes and Suggestions.

1. The notes of the preceding experiment (Cobalt) apply equally well to *nickel* and its compounds, and should be thoroughly reviewed in connection with the Nickel experiment.

2. No more ammonium sulphide should be used for the purpose of precipitating nickel sulphide than is absolutely necessary, since the precipitate is somewhat soluble in excess of the reagent, even in the presence of ammonium chloride, forming a dark-colored solution. In case this should occur, as indicated by the appearance of the filtrate, acidulate the filtrate with dilute hydrochloric acid, boil several minutes, and add the resulting precipitate to the main portion of nickel sulphide.

Scheme 9. — Zinc, Manganese, Cobalt, Nickel.

Devise and state a scheme for the separation and determination of *Zinc*, *Manganese*, *Cobalt*, and *Nickel*, in solution of their salts.

Experiment 30. — Zinc, Manganese, Cobalt, Nickel.

Take 10 cc. solution containing zinc nitrate, $Zn(NO_3)_2$, manganese nitrate, $Mn(NO_3)_2$, cobalt nitrate, $Co(NO_3)_2$, and nickel nitrate, $Ni(NO_3)_2$. Separate and determine as *per Scheme 9.*

Notes and Suggestions.

1. The separation of *zinc* and *manganese* from *cobalt* and *nickel* by means of cold dilute hydrochloric acid may be advantageously done on the filter paper, by pouring the same portion of the reagent over the filter several times in quick succession.

2. Traces of the sulphides of *cobalt* and *nickel* are likely to be dissolved by hydrochloric acid and reprecipitated by caustic potash as hydroxides, mixed with the manganese hydroxide. Their presence, however, will not interfere with the determination of *manganese*.

3. Before undertaking this experiment all instructions, notes, and suggestions pertaining to the experiments of the fourth group should be thoroughly reviewed and memorized. Difficulties must be anticipated in order that they may be avoided or overcome, and here, as elsewhere, an intelligent understanding of processes, not empirical method, is the only guarantee of success.

Some Reactions in Group IV.

Balance these equations: —

1. $Zn + HNO_3 = Zn(NO_3)_2 + NO + H_2O.$
2. $Zn(NO_3)_2 + NH_4OH = (NH_4)_2ZnO_2 + NH_4NO_3 + H_2O.$
3. $ZnS + HCl + (NH_4)_2S = \underline{ZnS} + NH_4Cl + H_2S.$
4. $ZnS + HCl = ZnCl_2 + H_2S.$
5. $ZnCl_2 + KOH = \underline{Zn(OH)_2} + KCl.$
6. $Zn(OH)_2 + KOH = K_2ZnO_2 + H_2O.$
7. $K_2ZnO_2 + HC_2H_3O_2 = Zn(C_2H_3O_2)_2 + KC_2H_3O_2 + H_2O.$
8. $Zn(C_2H_3O_2)_2 + H_2S = \underline{ZnS} + HC_2H_3O_2.$
9. $MnO_2 + HCl = MnCl_2 + Cl + H_2O.$
10. $Mn(NO_3)_2 + NH_4OH = Mn(NO_3)_2NH_4NO_3 + Mn(OH)_2.$
11. $MnCl_2 + (NH_4)_2S = \underline{MnS} + NH_4Cl.$

12. $MnS + HCl = MnCl_2 + H_2S.$

13. $MnCl_2 + KOH = \underline{Mn(OH)_2} + KCl.$

14. $Mn(OH)_2 + KNO_3 + Na_2CO_3 = K_2MnO_4 + Na_2MnO_4$
$+ NO + CO_2 + H_2O.$

15. $CoCl_2 + KNO_2 + HC_2H_3O_2 + H_2O = KCl$
$+ \underline{(KNO_2)_3Co(NO_2)_3\,2\,H_2O} + KC_2H_3O_2 + NO.$

16. $NiCl_2 + NaOH = \underline{Ni(OH)_2} + NaCl.$

The precipitates are underscored.

GROUP V.

BARIUM, CALCIUM, STRONTIUM.

General Remarks. — The fifth group includes those metals not found in the preceding groups whose carbonates are insoluble in the presence of ammonium salts. They are precipitated by ammonium carbonate in the presence of ammonium hydroxide and ammonium chloride.

Experiment 31. — Barium.

(*a*) Take 5 cc. solution of barium nitrate, $Ba(NO_3)_2$. Add dilute hydrochloric acid. Is there any precipitate? Pass in a small quantity of hydrogen sulphide. Is there any precipitate? Boil to expel hydrogen sulphide. Add a few drops of concentrated nitric acid. Add ammonium chloride and ammonium hydroxide, as in experiment 22 (*d*). Is there any precipitate? Add a few drops of ammonium sulphide, $(NH_4)_2S$. Is there any precipitate?

(*b*) Add ammonium carbonate, $(NH_4)_2CO_3$, drop by drop, to complete precipitation, and heat gently for some time, *but not to boiling*. The white precipitate formed is barium carbonate, $BaCO_3$. Set aside until the supernatant liquid is clear. Add one drop of ammonium carbonate. If this produces a precipitate, more ammonium carbonate must be added, and the heating repeated. This operation must be repeated until no precipitate is formed upon the addition of ammonium carbonate.

(*c*) Filter and wash thoroughly, collecting the precipitate in the apex of the filter paper. Dissolve in the least neces-

sary quantity of warm acetic acid, using but a few drops at a time, and pouring the filtrate repeatedly upon the filter paper. Finally, clear the filter paper of the adhering solution with a little water, and collect with the filtrate.

(*d*) Boil the filtrate, and add potassium dichromate solution, $K_2Cr_2O_7$, until no further precipitate is formed and the supernatant liquid appears orange-red.

(*e*) The formation of the pale yellow precipitate of barium chromate, $BaCrO_4$, *indicates the presence of Barium.*

(*f*) Confirm the test for *Barium* by filtering the precipitate obtained in (*d*), washing, dissolving in dilute hydrochloric acid, and adding dilute sulphuric acid. A heavy, white, finely pulverulent precipitate of barium sulphate, $BaSO_4$, confirms the test.

SUPPLEMENTARY. — 1. To 5 cc. solution of barium nitrate add a small quantity of sodium phosphate, Na_2HPO_4. A white precipitate of barium hydrogen phosphate, $BaHPO_4$, is thrown down. Add hydrochloric acid. The precipitate is dissolved.

2. To 5 cc. solution of barium nitrate add a small quantity of ammonium oxalate, $(NH_4)_2C_2O_4$. A white pulverulent precipitate of barium oxalate, BaC_2O_4, is produced. Add hydrochloric acid. The precipitate is dissolved.

3. Dip the loop of a platinum wire into some barium nitrate, and hold in the Bunsen flame. A green coloration is produced.

Notes and Suggestions.

1. Since barium carbonate is slightly soluble in ammonium chloride, especially when heated, a large excess of that reagent should be avoided. In fact, in a highly dilute solution of a *barium* salt, ammonium carbonate may fail to produce any precipitate whatever in the presence of ammonium chloride. If, for any reason, the solution is thought to be dilute, it should be concentrated by evaporation before adding the ammonium carbonate. The presence of ammonium hydroxide, however, rather promotes the precipitation.

2. Excess of acetic acid must be avoided in (*c*), since barium chromate will not precipitate completely in its presence.

Experiment 32. — Calcium.

(*a*) Repeat Experiment 31, using calcium nitrate, $Ca(NO_3)_2$, instead of barium nitrate, $Ba(NO_3)_2$, proceeding as far as (*c*). Is any precipitate formed upon the addition of ammonium carbonate? Proceed to (*d*). Does the precipitate dissolve in acetic acid? Proceed to (*e*). Does potassium dichromate produce any precipitate?

(*b*) Add ammonium hydroxide to the solution to alkaline reaction.

(*c*) Add ammonium carbonate, as in Experiment 31 (*b*). Filter. Collect the precipitate in the apex of the filter paper. Wash until the potassium dichromate is entirely removed, and the *wash water runs colorless.*

(*d*) Dissolve in the least necessary quantity of nitric acid. Evaporate the solution to dryness slowly over a low flame. Rub the residue, calcium nitrate, to a fine powder in the evaporating dish, and digest for several minutes with 10 cc. of absolute alcohol, or, quite as good, boil with amyl alcohol.

(*e*) The calcium nitrate dissolves. Add a few drops of dilute sulphuric acid. A white precipitate of calcium sulphate, $CaSO_4$, soluble in strong (ammoniacal) solution of ammonium sulphate, $(NH_4)_2SO_4$, *proves the presence of Calcium.*

SUPPLEMENTARY. — 1. To 5 cc. solution of calcium nitrate add a small quantity of ammonium oxalate, $(NH_4)_2C_2O_4$. A white precipitate of calcium oxalate, CaC_2O_4, is thrown down. This precipitate is soluble in dilute hydrochloric or nitric acid but insoluble in acetic acid, $HC_2H_3O_2$.

2. To 5 cc. solution of calcium nitrate add a small quantity of sodium phosphate, Na_2HPO_4. A white precipitate of calcium hydrogen phosphate, $CaHPO_4$, is thrown down. Add hydrochloric acid. The precipitate dissolves.

3. Moisten some solid calcium nitrate with hydrochloric acid, an introduce into a Bunsen flame on the loop of a platinum wire. A du red coloration is produced.

Notes and Suggestions.

1. The notes appended to the Barium Experiment apply equally we to *calcium*, and should be reviewed in this connection.

2. Calcium sulphate is somewhat soluble in water, but insoluble i alcohol.

3. When the proportion of *calcium* in a solution is small, the precipitate produced in (*c*) by ammonium carbonate is liable to be obscure by the red color of the potassium dichromate, although the subseque filtration is quite certain to reveal it.

4. It is necessary that the heating of the calcium nitrate in (*d*) b sufficiently prolonged to render it completely anhydrous. The temperature may reach 180°, although if much higher it will change th nitrate to an oxide, which is insoluble in alcohol. Since the nitrat is deliquescent, it should be treated with the alcohol immediately aft dehydration.

Experiment 33. — Strontium.

(*a*) Repeat Experiment 32, using solution of strontiu nitrate, $Sr(NO_3)_2$, instead of calcium nitrate, $Ca(NO_3$ proceeding as far as (*b*). Is strontium carbonate, SrCO soluble in acetic acid? Is any precipitate formed upon th addition of potassium dichromate? Proceed to (*e*). Doe the strontium nitrate dissolve in alcohol?

(*b*) Filter and wash with alcohol. Place the filter pape with strontium nitrate upon it in the evaporating dish Add about 2 cc. of water, and warm gently to dissolve th precipitate. Pour the solution into a test-tube, add a smal quantity of calcium sulphate solution, and heat gently The formation of a white pulverulent precipitate, strontium sulphate, $SrSO_4$, *indicates the presence of Strontium.* I

the case of a very dilute solution, the precipitate may form only after some time.

(*c*) Confirm the test for *Strontium* by introducing a portion of the final precipitate in (b) into the reducing flame on a platinum wire. The strontium sulphate is converted into the sulphide. Moisten the sample with hydrochloric acid, and again bring into the flame. *An intensely red or crimson coloration is produced.*

(*d*) Upon what fact does the separation of *Barium*, *Calcium*, and *Strontium* from the first group depend? from the second group? from the third group? from the fourth group?

(*e*) Upon what fact does the separation of *Calcium* and *Barium* depend? *Strontium* and *Barium?* *Strontium* and *Calcium?*

SUPPLEMENTARY. — 1. To 5 cc. solution of strontium nitrate add a small quantity of ammonium oxalate. White strontium oxalate, SrC_2O_4, is precipitated, soluble in dilute hydrochloric or nitric acid, but sparingly soluble in acetic acid.

2. Introduce a small quantity of solid strontium nitrate, previously moistened with hydrochloric acid, into the edge of the Bunsen flame on a platinum wire. A crimson coloration is produced.

3. To 5 cc. solution of strontium nitrate add a small quantity of sodium phosphate, Na_2HPO_4. A white precipitate of strontium hydrogen phosphate, $SrHPO_4$, is thrown down. Add hydrochloric acid. The precipitate dissolves.

Notes and Suggestions.

1. Although strontium carbonate is less soluble than barium carbonate in ammonium chloride, the precautions recommended in the notes of the Barium Experiment should receive equal attention here.

2. Strontium sulphate is less soluble than calcium sulphate, while barium sulphate is insoluble. Strontium sulphate, however, is insoluble in alcohol.

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Scheme 10.—Barium, Calcium, Strontium.

Devise and state a scheme for the separation and determination of *Barium*, *Calcium*, and *Strontium* in solution of their salts.

Experiment 34.—Barium, Calcium, Strontium.

Take 10 cc. solution containing barium nitrate, $Ba(NO_3)_2$, calcium nitrate, $Ca(NO_3)_2$, and strontium nitrate, $Sr(NO_3)_2$. Separate and determine as per Scheme 10.

SUPPLEMENTARY.—1. Take 10 cc. solution containing barium nitrate, calcium nitrate, and strontium nitrate. Treat the solution as in Experiment 31, proceeding to (*f*). The formation of a precipitate indicates *barium*. Confirm the test as in Experiment 31 (*f*). Treat the filtrate from (*f*) as in Experiment 32 (*b*) and (*c*). *Strontium* and *calcium* are once more precipitated as carbonates. Dissolve the precipitate in acetic acid exactly as instructed in Experiment 31 (*c*). Divide the solution into two portions. To one add solution of calcium sulphate, heat, and allow to stand 10 minutes. A white, finely pulverulent precipitate indicates *strontium*. Confirm the test as in Experiment 33 (*c*). To the second portion of the acetic acid solution add solution of potassium sulphate, boil, and let stand until cool. Strontium sulphate is thrown down, probably mixed with some calcium sulphate. Filter, and to the filtrate add solution of ammonium oxalate. A white precipitate, insoluble in the acetic acid present, but soluble in hydrochloric acid, proves the presence of *calcium*.

Notes and Suggestions.

1. Acetic acid is used in this group in order to furnish a suitable medium for the separation of *barium* from the other members of the group. The *barium* is precipitated by potassium dichromate as barium chromate, nearly insoluble in acetic acid, while *calcium* and *strontium* remain in solution.

2. The barium chromate must be completely removed (by repeated filtration, if necessary) before proceeding to the determination of *calcium and strontium*, since its presence would render the test for *strontium unreliable*.

3. So far as the separation and determination of the members of the fifth group is concerned, it is obviously unnecessary to add hydrochloric acid, hydrogen sulphide, nitric acid, ammonium chloride, and ammonium sulphide, as instructed in Experiment 31 (*a*). They are introduced chiefly for the purpose of indicating the points of separation of this group from the preceding groups, and because in the practical analysis of unknown substances they would necessarily be present in greater or less quantities. Their deportment, therefore, is an important factor to be considered.

Some Reactions in Group V.

Balance these equations: —

1. $BaCO_3 + HC_2H_3O_2 = Ba(C_2H_3O_2)_2 + H_2O + CO_2$.
2. $Ba(C_2H_3O_2)_2 + H_2O + K_2Cr_2O_7$
   $= \underline{BaCrO_4} + KC_2H_3O_2 + HC_2H_3O_2$.
3. $CaCO_3 + HC_2H_3O_2 = Ca(C_2H_3O_2)_2 + H_2O + CO_2$.
4. $Ca(C_2H_3O_2)_2 + (NH_4)_2CO_3 = \underline{CaCO_3} + NH_4C_2H_3O_2$.
5. $CaCO_3 + HNO_3 = Ca(NO_3)_2 + H_2O + CO_2$.
6. $Ca(NO_3)_2 + H_2SO_4 = \underline{CaSO_4} + HNO_3$.
7. $SrCO_3 + HC_2H_3O_2 = Sr(C_2H_3O_2)_2 + H_2O + CO_2$.
8. $Sr(C_2H_3O_2)_2 + (NH_4)_2CO_3 = \underline{SrCO_3} + NH_4C_2H_3O_2$.
9. $SrCO_3 + HNO_3 = Sr(NO_3)_2 + H_2O + CO_2$.
10. $Sr(NO_3)_2 + K_2SO_4 = KNO_3 + \underline{SrSO_4}$.

The precipitates are underscored.

GROUP VI.

MAGNESIUM, SODIUM, POTASSIUM, AMMONIUM.

General Remarks. — The sixth group includes tho metals which are not precipitated from their solutions l the preceding group reagents, and which have no comm precipitant. They must therefore be tested for individual

Experiment 35. — Magnesium.

(*a*) Take 5 cc. solution of magnesium nitrate, Mg(NO$_3$ Add dilute hydrochloric acid. Is there any precipitat Pass in a small quantity of hydrogen sulphide. Is the any precipitate? Boil to expel hydrogen sulphide. Ad a few drops of concentrated nitric acid. Add ammoniu chloride and ammonium hydroxide, as in Experiment 22(*d* Is there any precipitate? Add a few drops of ammoniu sulphide, $(NH_4)_2S$. Is there any precipitate? Add a fe drops of ammonium carbonate, and heat gently for a fe minutes. Is there any precipitate?

(*b*) Evaporate the liquid to small bulk, and set aside i a test-tube to cool.

(*c*) When cold add a few drops of sodium phospha solution, Na_2HPO_4, and as much ammonium hydroxide, a shake at frequent intervals. A white *crystalline* preci tate of the double phosphate of magnesium and ammoniu $MgNH_4PO_4$, *proves the presence of Magnesium.*

(*d*) Upon what fact does the separation of *Magnesiu* the first group metals depend? from the seco

group? from the third group? from the fourth group? from the fifth group?

SUPPLEMENTARY. — 1. To 5 cc. neutral solution of magnesium nitrate add a small quantity of ammonium hydroxide. Magnesium hydroxide, $Mg(OH)_2$, is partially precipitated. Now add a small quantity of ammonium chloride solution. The hydroxide readily dissolves.

2. Heat a small quantity of solid magnesium nitrate on charcoal in the blow-pipe flame, then moisten with solution of cobalt nitrate, and heat again. A pink mass is obtained when cool.

3. To 5 cc. solution of magnesium nitrate add a small quantity of ammonium carbonate. A white precipitate of magnesium carbonate, $MgCO_3$, is produced. Add ammonium chloride solution. The precipitate dissolves.

4. To 5 cc. solution of magnesium nitrate add a small quantity of barium hydroxide, $Ba(OH)_2$. Magnesium hydroxide is precipitated. Add ammonium chloride solution. The precipitate dissolves.

Notes and Suggestions.

1. But for the presence of ammonium chloride, precipitates would be produced in (*a*) both by ammonium hydroxide and ammonium carbonate.

2. In the absence of ammonia and ammonium salts, sodium phosphate precipitates from *magnesium* solutions, if they are not too dilute, magnesium hydrogen phosphate, $MgHPO_4$. In the presence of ammonia and ammonium chloride, however, a precipitate of magnesium ammonium phosphate will separate, even in very dilute solutions, although as much as twenty-four hours may be required for it to crystallize. The double phosphate is distinguished by its crystalline character, which can be determined by using a microscope, and also by the peculiar manner in which it gathers on the test-tube when rubbed on the inner side with a glass rod.

Experiment 36. — Sodium.

(*a*) Repeat Experiment 35, using solution of sodium *nitrate*, $NaNO_3$, instead of magnesium nitrate, $Mg(NO_3)_2$, *proceeding* as far as (*b*).

(*b*) Evaporate to dryness, and ignite the residue gently to drive off ammonium chloride, being careful to continue until fuming ceases. Cool. Add three or four drops of water.

(*c*) Clean the loop of a platinum wire by washing and heating until it ceases to impart any color to the flame. Dip the loop into the solution and again hold it in the flame. *An intense yellow color proves the presence of Sodium.*

Notes and Suggestions.

1. None of the common reagents give characteristic reactions with solutions of sodium compounds, since nearly all sodium salts are soluble in water. The flame test alone, therefore, is ordinarily used to distinguish this metal. Since traces of *sodium* compounds may be found in most reagents, some experience will be required to determine whether the *sodium* indicated is present as an accidental impurity or in considerable quantity.

Experiment 37. — Potassium.

(*a*) Repeat Experiment 36, using solution of potassium nitrate, KNO_3, instead of sodium nitrate, $NaNO_3$, proceeding as far as (*c*).

(*b*) Clean the loop of a platinum wire by washing and heating, dip it into the solution, and hold in the flame, looking at the flame through a piece of deep-blue cobalt glass. The *reddish-violet coloration imparted to the flame proves the presence of Potassium.*

(*c*) To the remainder of the solution add about 1 cc. of hydrochloroplatinic acid, H_2PtCl_6. A yellow crystalline precipitate of potassium platini-chloride, K_2PtCl_6, is produced, *confirming the presence of Potassium.*

SUPPLEMENTARY. — 1. To 5 cc. solution of potassium nitrate add *small quantity* of tartaric acid, $H_2C_4H_4O_6$. A white granular-crystallin

precipitate of hydrogen potassium tartrate, $HKC_4H_4O_6$, is formed. The precipitation is promoted by agitation and the addition of a little alcohol.

Notes and Suggestions.

1. It is important that the blue glass used in this experiment should be of moderate thickness, and colored blue throughout, not merely flashed. The use of the blue glass is to exclude possible yellow sodium light, which might overpower and obscure the violet rays.

2. The test advised in (*c*) for *potassium* is unreliable unless ammonium salts have been completely removed by ignition, since their reaction with hydrochloroplatinic acid is similar to that of *potassium*.

3. In case no precipitate should form in (*c*) within fifteen minutes, evaporate the solution *nearly to dryness*, and pour a little alcohol over the residue. The yellow potassium platini-chloride will be left undissolved.

Experiment 38. — Ammonium.

Remarks. — In testing for *Ammonium* the original substance or solution must be examined, since it enters into many of the reagents used in the course of analysis in the preceding groups.

Procedure. — (*a*) To 5 cc. solution of ammonium nitrate, NH_4NO_3, add about 1 cc. solution of caustic soda in a test-tube, and heat. Ammonia will be evolved. Note the odor. Note the effect on red litmus paper held in the mouth of the tube. Moisten a stirring rod with hydrochloric acid and hold it in the mouth of the test-tube. Dense white fumes will arise.

(*b*) Heat a small quantity of solid ammonium nitrate on charcoal before the blow-pipe. It should volatilize completely.

(*c*) Evaporate 5 cc. solution of ammonium nitrate barely to dryness. Mix with an equal quantity of freshly slaked lime, transfer to a test-tube, and slightly moisten. Heat

gently, and test the escaping gas with litmus and hydrochloric acid, as in (*a*).

Experiment 39.—Magnesium, Sodium, Potassium, Ammonium.

(*a*) Take 10 cc. solution containing magnesium nitrate, $Mg(NO_3)_2$, sodium nitrate, $NaNO_3$, potassium nitrate, KNO_3, and ammonium nitrate, NH_4NO_3. With a portion of it test for *Ammonium* as in Experiment 38 (*a* and *c*).

(*b*) Treat the remaining portion as in Experiment 35, proceeding as far as (*c*). Divide the concentrated solution into two parts.

(*c*) Treat one part of the solution as in Experiment 35 (*c*), and prove the presence of *Magnesium*.

(*d*) Evaporate the other part of the solution to dryness, ignite *gently* until all fuming ceases, to drive off *Ammonium* salts, dissolve in water, and add barium hydroxide until the solution is alkaline. Magnesium hydroxide will be precipitated. Boil and filter. To the filtrate add ammonium carbonate. Barium carbonate is precipitated. Heat and filter. Evaporate the filtrate to dryness, ignite carefully, and dissolve in a few drops of water. The solution now contains only *Sodium* and *Potassium* salts.

(*e*) With a portion of the solution from (*d*) test for *Sodium* as in Experiment 36 (*c*).

(*f*) With another portion of the solution test for *Potassium* as in Experiment 37 (*b* and *c*).

Notes and Suggestions.

1. The object of the somewhat tedious operations in (*d*) is to free the solution from *ammonium* and *magnesium*, both of which interfere more or less with the tests for *sodium* and *potassium*.

2. The ignition should be conducted very carefully, at a low heat, to avoid the possible decomposition of the *sodium* and *potassi* salts.

3. It is advised by some to use ammonium phosphate, $(NH_4)_2HP$ instead of barium hydroxide for eliminating the *magnesium.* In t event, the following procedure would be substituted for that in (*d*): the other part of the solution add ammonium phosphate to comp precipitation. Filter, concentrate the filtrate by evaporation, and for *sodium* as in Experiment 36 (*c*) and for *potassium* as in Exp ment 37 (*b*).

Some Reactions in Group VI.

Balance these equations: —

1. $Mg(NO_3)_2 + NaOH = \underline{Mg(OH)_2} + NaNO_3$.
2. $Mg(NO_3)_2 + Na_2HPO_4 + NH_4OH$
   $= \underline{MgNH_4PO_4} + Na_2SO_4 + H_2$
3. $KCl + H_2PtCl_6 = \underline{K_2PtCl_6} + HCl$.
4. $NH_4Cl + H_2PtCl_6 = \underline{(NH_4)_2PtCl_6} + HCl$.
5. $NH_4NO_3 + Ca(OH)_2 = Ca(NO_3)_2 + NH_3 + H_2O$.
6. $NH_4NO_3 + NaOH = NaNO_3 + NH_3 + H_2O$.
7. $Mg(NO_3)_2 + Na_2CO_3 + H_2O$
   $= NaNO_3 + CO_2 + \underline{Mg_4(OH)_2(CO}$

The precipitates are underscored.

Experiment 40. — Detection of Bases in Aqueous Soluti of Unknown Composition.

General Remarks. — Having learned the tests e ployed to determine the presence of the twenty-th metals embraced within the scope of this manual, t student is now prepared to undertake the analysis *a solution of* unknown composition. It should be bo

in mind that this work must proceed systematically, fr the first to the sixth group, each group being carefu and completely eliminated by its proper reagent bef proceeding to the next one. It is an incidental advanta to know that if a group reagent fails to produce a preci tate, it is unnecessary to search for the individual me bers of the group. Of course it should be assumed tl any one or all of the metals may be present in the mixt to be analyzed, although a study of the Table of Solub ties will show the improbability, in most instances, of th being more than a very limited number present in any c solution. The possibilities depend upon the nature of t solvent and the classes of salts in the mixture.

Procedure.—(*a*) Take 20 cc. solution containing memb of each of the groups of metals. Examine a small porti of the solution for ammonium as in Experiment 38 (*a*) a (*c*). Test small portions for iron, as in the supplementa part of Experiment 22 (2) and (7), to determine whet this metal, if present, is in the ferr*ous* or ferr*ic* conditi To the remainder add dilute hydrochloric acid, little little, to complete precipitation. The first group met will be precipitated. Filter and wash. Save the filtrat

(*b*) Examine the residue on the filter paper for fi group metals, as in Experiment 5 (*b*), (*c*), (*d*).

(*c*) Heat the filtrate from (*a*), and add hydrogen s phide to complete precipitation. [Read Note 4, Expe ment 8.] The second group metals will be precipitat Filter and wash thoroughly. Save the filtrate.

(*d*) Examine the precipitate from (*c*) for second gro metals, as in Experiment 21 (*b*).

(*e*) Treat the filtrate from (*c*) as in Experiment 22 and (*d*). The third group metals will be precipitat *Filter and* wash thoroughly. Save the filtrate.

(*f*) Examine the precipitate from (*e*) for third group metals, as in Experiment 25, beginning at the point in (*a*) where the hydroxides are being washed on the filter paper.

(*g*) Heat the filtrate from (*e*) to boiling, and add ammonium sulphide, *drop by drop*, to complete precipitation. The fourth group metals will be precipitated. Filter and wash. Save the filtrate.

(*h*) Examine the precipitate from (*g*) for fourth group metals, as in Experiment 30, beginning at the point where the sulphides of this group have just been precipitated, filtered, and washed.

(*i*) Concentrate the filtrate from (*g*) by evaporation, and then treat as in experiment 31 (*b*). The fifth group metals will be precipitated. Filter and wash. Save the filtrate.

(*j*) Examine the precipitate from (*i*) for fifth group metals, as in Experiment 34, beginning at the point where the carbonates of this group have just been precipitated, filtered, and washed.

(*k*) Treat the filtrate from (*i*) as in experiment 35 (*b*). Divide into two parts. Examine one part for *Magnesium*, as in Experiment 35 (*c*). Examine the other part for *Sodium* and *Potassium*, as in Experiment 39 (*d*), (*e*), and (*f*).

Notes and Suggestions.

1. Oxychlorides of *bismuth* and *antimony* may be thrown down in (*a*), but will redissolve in a slight excess of hydrochloric acid.

2. It is advisable to add hydrogen sulphide to a few drops of the filtrate in (*c*), from which the first group metals have been removed, before saturating the main solution. If no precipitate is formed, pass at once to (*e*).

3. If arsen*ic* compounds should be present, they will be but partially precipitated in (*c*) by hydrogen sulphide, until first reduced to the arsen*ious* condition. This requires prolonged heating, oftentimes several *hours, and repeated* saturations with hydrogen sulphide.

4. If the precipitate in (*d*) is reasonably large, it is advantageous to first treat a small portion of it with yellow ammonium sulphide, $(NH_4)_2S_x$, to determine whether members of division A are present. If so, treat the remainder of the precipitate in the same way. If absent, proceed to examine it for division B as in Experiment 20.

5. Since *manganese* and *zinc* are liable to be precipitated with the third group in (*e*), it is advisable to redissolve the precipitate in hydrochloric acid, and reprecipitate with ammonium chloride and ammonium hydroxide, repeating the process, if necessary, until the filtrate gives no precipitate with ammonium sulphide. The several filtrates may be combined with the one from (*e*).

6. Test a few drops of the filtrate in (*g*), from which the first three groups of metals have been removed, with ammonium sulphide, before adding it to the main portion. If no precipitate is formed, pass to (*i*).

7. In case the filtrate from (*g*) is dark colored, probably indicating *nickel*, acidulate with hydrochloric acid, boil, filter, and combine the precipitate with that in (*g*). The filtrate should again be made alkaline with ammonium hydroxide before continuing.

8. In case there is reason to suspect the presence of *phosphates*, *oxalates*, *silicates*, *fluorides*, or non-volatile *organic* bodies, the scheme outlined above for the separation of the third, fourth, fifth, and sixth groups of metals must be departed from to some extent, for the reasons stated on p. 70. After the elimination of the first two groups, the next proceeding is to determine positively whether or not the filtrate from (*c*) contains *phosphoric acid*. This is best done by following the instructions in Experiment 44, using 2 cc. of the filtrate to be tested instead of the sodium phosphate, Na_2HPO_4.

A. PROCEDURE IN PRESENCE OF PHOSPHATES.

(*a*) Treat the filtrate from Experiment 40 (*c*) as in Experiment 22 (*c*) and (*d*). Filter, and wash thoroughly. Save the filtrate.

(*b*) To the filtrate from (*a*) add ammonium sulphide, as directed in Experiment 40 (*g*). Filter and wash, adding a little ammonium sulphide to the wash water. Save the filtrate.

(*c*) Examine the filtrate from (*b*) for fifth and sixth groups of metals exactly as directed in Experiment 40 (*i*), (*j*), and (*k*).

(*d*) Combine the precipitates from (*a*) and (*b*), and digest in an evaporating dish with ammonium sulphide. Filter and wash. The

precipitate may contain hydroxides and phosphates of aluminum and chromium, sulphides of iron, manganese, cobalt, nickel, and zinc, and phosphates of barium, strontium, calcium, and magnesium.

(*e*) Transfer the precipitate from (*d*) to a test-tube, and dissolve in hot dilute hydrochloric acid, adding a *small particle* of potassium chlorate, $KClO_3$. Heat to expel all free chlorine, and filter to rid the solution of sulphur. Add dilute solution of sodium carbonate, a little at a time, until *very nearly* neutral, and then sodium acetate, $NaC_2H_3O_2$, strongly acidified with acetic acid, $HC_2H_3O_2$, to complete precipitation. Digest for some time at a gentle heat, and filter hot. Save the filtrate.

(*f*) The precipitate from (*e*) may contain iron phosphate, $FePO_4$, aluminum phosphate, $AlPO_4$, and chromium phosphate, $CrPO_4$. Transfer to an evaporating dish, cover with strong caustic soda or caustic potash solution (free from aluminum) and boil for several minutes. Aluminum phosphate will dissolve; iron and chromium phosphates will not. Dilute with a considerable quantity of water, and filter. Wash thoroughly. Save the filtrate.

(*g*) Test the filtrate from (*f*) for *aluminum* as in Experiment 23 (*b*). With a portion of the precipitate from (*f*) test for *chromium* as in Experiment 24 (*b*). With the remainder test for *iron* as in Experiment 22 (*g*) and (*h*).

(*h*) The filtrate from (*e*) may contain chlorides of iron, aluminum, chromium, zinc, manganese, cobalt, nickel, barium, calcium, strontium, and magnesium, and, in the absence of third-group metals, free phosphoric acid. Concentrate it by evaporation, and cautiously add solution of ferric chloride, *drop by drop*, as long as a precipitate forms, or until a drop of the solution gives a buff-colored precipitate with ammonium hydroxide. Digest at a gentle heat for some time, and filter. The precipitate is iron phosphate, $FePO_4$, and may be rejected. Save the filtrate.

(*i*) Examine the filtrate from (*h*), which is now free from phosphoric acid, for the third, fourth, and fifth groups of metals, as directed in Experiment 40 (*e*), (*f*), (*g*), etc.

B. PROCEDURE IN PRESENCE OF OXALATES.

(*a*) The presence of *oxalates* may be determined by applying the test suggested in Experiment 46 (*c*), using a small portion of the filtrate from Experiment 40 (*c*) instead of oxalic acid, $C_2H_2O_4$. The method of

analysis employed in the presence of *phosphates* (see *A*) will answer also for *oxalates*, since the deportments of these compounds are quite similar; but if the ignition and oxidation advised in (*C*) be employed, the *oxalates* will be completely decomposed.

C. PROCEDURE IN PRESENCE OF SILICATES, FLUORIDES, OR ORGANIC MATTER.

(*a*) If *silicates*, *fluorides*, or non-volatile *organic* bodies are present, it is a wise precaution to eliminate them by ignition and oxidation before attempting the separation of the third group. First test a small portion of the filtrate from the second group by evaporating to dryness and heating the residue in a closed tube to which is attached a small rubber delivery tube. Conduct any gas that may be evolved into lime water. If there is considerable charring or blackening of the residue, accompanied by the formation of a white precipitate in the lime water, organic matter is probably present. If a white residue remains that is insoluble in hydrochloric acid, it is probably *silica* or *calcium fluoride*. To remove these substances proceed as follows:—

Evaporate the filtrate from the second group to dryness. Ignite at a low temperature in a porcelain crucible until the substance is charred. Cool, moisten with a few drops of strong nitric acid, evaporate, ignite *very gently* at first and then strongly. Repeat the addition of nitric acid and the ignition until no carbon remains. Boil the residue with a little concentrated hydrochloric acid, dilute, and filter. By this operation the *organic* matter will be destroyed, the *fluorine* expelled, and the *silica* left behind on the filter paper. In case chlorides are present, a little *iron* may be lost through volatilization. [See Notes under Part III., Sec. I., B.]

Experiment 41.—Analysis of Alloys and Pure Metals.

General Remarks.— Since all metals are soluble in some acid, their determination is attended with but little difficulty. If possible, a small portion of the substance should be reduced to powder by pulverizing in a mortar, or, if soft, it may be shaved. In some cases it may be reduced by melting in a crucible and shaking to a powder while still hot.

Procedure.—(*a*) 1. Take a quantity of the material equivalent to a pea in bulk, and put into a flask. Cover with concentrated nitric acid, and *heat gently* under the hood for fully half an hour, or until no further change takes place, replacing from time to time the acid lost by evaporation. Dilute the liquid with two or three times its volume of water, and heat some time longer. If complete solution takes place, this proves the absence of *Gold, Platinum, Antimony,* and *Tin.*

2. Evaporate the solution in an evaporating dish nearly to dryness to get rid of the greater part of free nitric acid, and then add about ten times its volume of water. If the liquid should be turbid, or a precipitate form, *Bismuth* is probably present. In this event, add sufficient nitric acid barely to clear the fluid. Proceed with the analysis as in Experiment 40.

(*b*) If a metallic residue remains after treatment with the nitric acid, filter and treat the filtrate as directed in (*a*) 2, first evaporating a drop or two to dryness on platinum foil to determine whether anything has really been dissolved. The metallic residue must be *Gold* or *Platinum.* Wash thoroughly, and dissolve in aqua regia. Evaporate to small bulk and proceed with the following tests:—

Test for Gold.—Dilute a portion of the liquid with ten times its volume of water, and pour into a beaker placed on a sheet of white paper. Prepare a mixture of stannous and stannic chlorides by adding to one or two cubic centimeters of the former a few drops of ferric chloride or of chlorine water. Dip a stirring rod first into the tin solution and then into the one to be tested for *Gold.* A blue or purplish streak will be observed in the trail of the rod, if even a trace of the precious metal is present. This peculiar product is known as "Purple of Cassius."

Test for Platinum. — To a portion of the concentrated liquid add a small quantity of a cold saturated solution of ammonium chloride. The formation of a yellow, crystalline precipitate of ammonium platini-chloride, $(NH_4)_2PtCl_6$, shows the presence of *Platinum*. The test may be made more delicate by the addition of a little alcohol, since the platini-chloride is less soluble in alcohol than in water.

(*c*) If a white pulverulent residue remains from (*a*) after treatment with nitric acid, it is probably oxide of *Tin* or *Antimony*, or both, or possibly arsenates of those metals. Filter, and treat the filtrate as suggested in (*a*) 2, after determining whether anything has gone into solution. Wash the residue thoroughly. Digest in boiling concentrated hydrochloric acid for ten minutes, dilute with water, and test for *Antimony*, *Tin*, and *Arsenic*, as in Experiment 13.

(*d*) If the residue remaining from (*a*) contains both a metallic substance and a white powder, filter, and treat the filtrate as suggested in (*a*) 2. Wash the residue thoroughly, remove to an evaporating dish, and treat with boiling concentrated hydrochloric acid for several minutes. Dilute with water, and filter. Test the filtrate for *Antimony*, *Tin*, and *Arsenic* as in Experiment 13, and the residue for *Gold* and *Platinum* as in (*b*).

Notes and Suggestions.

1. Metallic *arsenic* and *antimony* are nearly insoluble in hydrochloric acid, while their oxides are soluble. It is necessary, then, that the digestion with nitric acid in (*a*) be continued until the oxidation of these metals is complete, since otherwise the treatment in (*c*) and (*d*) may fail to reveal them.

2. If *arsenic* is present, nitric acid will convert it in part into arsenic acid, some of which will combine with *antimony* and *tin*, forming

arsenates, which are insoluble in nitric acid, but soluble in hydrochloric acid. *Arsenic*, therefore, may be sought for in both the nitric and hydrochloric acid solutions.

3. In case more than one-fourth of the alloy consists of *gold* or *platinum*, nitric acid will fail to effect a complete disintegration. The best recourse is to reduce the percentage of *gold* or *platinum* by fusing the alloy with some metal whose presence or absence is positively known.

4. Since *barium*, *calcium*, *strontium*, and *chromium* are never present in alloys, all operations required for their detection may be omitted. *Sodium* and *potassium* need be looked for only when the alloy decomposes hot water.

5. In addition to the elements whose detection is provided for in Experiment 41, alloys may contain *phosphorus*, *carbon*, *silicon*, and some of the *rare metals* found in platinum ores. *Carbon* and *silicon* will remain as a black residue upon treating the alloy with nitric acid. The *rare metals* referred to will be found with the *platinum* residue in (*b*). *Phosphorus* may be present as phosphoric acid in either the nitric or hydrochloric acid solution, and should be tested for as in Experiment 44 (*a*).

PART II.

CHARACTERISTIC REACTIONS OF A FEW OF THE MORE COMMON ACIDS.

General Remarks. — It is not possible to group the acids with the same precision as the metals, although they may be approximately classified according to their behavior with certain reagents. For the purposes of this manual, twenty-two of the most important acids have been selected as representative of the several groups, and as the ones more commonly met with in the course of analysis. With but few exceptions, the salt of an acid gives the test of that acid, and in most of the preliminary experiments that follow salts and not the free acids are employed.

Experiment 42. — Grouping of the Acids.

(*a*) To 5 cc. solution of sodium sulphate, Na_2SO_4, add a few drops of barium chloride, $BaCl_2$. Barium sulphate, $BaSO_4$, is thrown down as a white precipitate. In the case of a very dilute solution the precipitate may be slow in forming. Filter and wash. Remove a portion of the precipitate to an evaporating dish, and try to dissolve it in dilute hydrochloric acid. Result? Try to dissolve another portion in dilute nitric acid. Result? Would barium chloride precipitate a sulphate in the presence of hydrochloric or nitric acid?

(*b*) To 5 cc. solution of sodium sulphate add a few drops of *silver nitrate*, $AgNO_3$. Result?

(*c*) Heat a small quantity of sodium sulphate to redness on a piece of porcelain. Is there any indication of charring?

(*d*) Repeat (*a*), (*b*), and (*c*), using the following salts and acids instead of sodium sulphate: Sodium phosphate, Na_2HPO_4; borax, $Na_2B_4O_7$; oxalic acid, $C_2H_2O_4$; ammonium fluoride, NH_4F; sodium carbonate, Na_2CO_3; sodium silicate, Na_2SiO_3; sodium sulphite, Na_2SO_3; sodium thiosulphate, $Na_2S_2O_3$; sodium arsenite, Na_3AsO_3; sodium arsenate, Na_3AsO_4; potassium chromate, K_2CrO_4; sodium chloride, NaCl; potassium bromide, KBr; potassium iodide, KI; potassium cyanide, KCN; potassium nitrite, KNO_2; sodium sulphide, Na_2S; potassium nitrate, KNO_3; potassium chlorate, $KClO_3$; potassium sodium tartrate, $KNaC_4H_4O_6$; and sodium acetate, $NaC_2H_3O_2$. Tabulate the results under the following heads:—

Group I.—Acids which are precipitated by barium chloride in *both neutral and acid solutions.*

Group II.—Acids which are precipitated by barium chloride in *neutral solutions only.*

Group III.—Acids which are precipitated in neutral solutions by silver nitrate and not by barium chloride.

Group IV.—Acids which are not precipitated by silver nitrate or barium chloride.

Group V.—Acids which, regardless of their deportment towards the preceding group reagents, are charred when heated to redness.

Notes and Suggestions.

1. The solution must be *neutral or very slightly alkaline* before applying the barium or silver test. It may be made so by the careful addition of ammonium hydroxide.

2. In the case of sodium silicate the barium chloride produces a

white precipitate, which, while not actually dissolved by hydrochloric acid, is decomposed by it, *silicic acid*, H_4SiO_4, being set free as a gelatinous precipitate.

3. After the group to which an acid belongs has been determined, it can be identified usually only by making special tests for all the acids of that group, upon separate portions of the original substance.

4. Although *oxalic acid* is an organic acid, it is commonly classed with the inorganic for the purposes of analysis, since its salts do not char.

5. Charring does not necessarily prove the presence of an organic *acid*. It may be due to other organic bodies.

6. The mere blackening of a substance upon heating, without the characteristic burnt odor, may be due to compounds of copper, cobalt, iron, or nickel.

7. Experiments requiring the use of potassium cyanide had best be done under the hood, and care should be exercised to avoid inhaling the escaping gases.

8. Very careful notes should be made descriptive of the reactions between the general reagents and the individual acids. These reactions are characteristic in many instances, and, if thoughtfully studied at this point, will assist materially in the subsequent analyses.

GROUP I (SULPHURIC ACID GROUP).

Remark. — This group includes those acids which are precipitated by barium chloride *in both neutral and acid solutions.*

Experiment 43. — Sulphuric Acid and Sulphates.

(*a*) The test employed in Experiment 42 (*a*) is sufficient to *prove the presence of Sulphuric acid.*

SUPPLEMENTARY. — 1. To 5 cc. solution of sodium sulphate, Na_2SO_4, add a small quantity of lead acetate, $Pb(C_2H_3O_2)_2$. A heavy white precipitate of lead sulphate, $PbSO_4$, will be thrown down. Decant. Add concentrated hydrochloric acid to the residue, and boil. It should dissolve. Cool. Lead chloride, $PbCl_2$, crystallizes out.

2. Fuse on charcoal a small portion of lead sulphate with the same quantity of sodium carbonate, using the reducing flame of the blow-pipe. Sodium sulphate and lead carbonate are first formed, but are partly reduced to sodium sulphide, lead oxide, and metallic lead. Crush a portion of the product with a drop of water on a bright silver coin. Result?

Notes and Suggestions.

1. In very dilute solutions barium chloride does not produce an immediate precipitate; but if the solution is allowed to stand, it becomes clouded, and ultimately the precipitate subsides. When formed in the cold, the precipitate is very fine, and difficult to separate by filtration. Digesting warm for several minutes will greatly facilitate the operation.

GROUP II (Phosphoric Acid Group).

PHOSPHORIC, BORIC, OXALIC, HYDROFLUORIC, CARBONIC, SILICIC, SULPHUROUS, THIOSULPHURIC, ARSENIOUS, ARSENIC, AND CHROMIC ACIDS.

Remark. — This group includes those acids which are precipitated by barium chloride *in neutral solutions only.*

Experiment 44. — Phosphoric Acid and Phosphates.

(*a*) To 2 cc. solution of sodium phosphate, Na_2HPO_4, add a few drops of concentrated nitric acid, and then 3 or 4 cc. solution of ammonium molybdate, $(NH_4)_2MoO_4$. A yellow coloration, and ultimately a canary-yellow precipitate of ammonium phospho-molybdate *proves the presence of Phosphoric acid.* Warming *slightly* is an aid to precipitation, though not usually necessary.

Supplementary. — 1. To 5 cc. solution of sodium phosphate add 2 cc. of ammonium hydroxide and then a small quantity of magnesia mixture ($MgSO_4$, NH_4OH, and NH_4Cl). A white crystalline precipitate of magnesium ammonium phosphate, $MgNH_4PO_4$, is produced, even in very dilute solutions, although often only after the lapse of some time. Stirring promotes the separation.

2. To 5 cc. solution of sodium phosphate add a small quantity of sodium acetate, $NaC_2H_3O_2$, and then solution of ferric chloride, $FeCl_3$, *drop by drop*, as long as a precipitate forms. Add hydrochloric acid. The precipitate, consisting of ferric phosphate, $FePO_4$, dissolves.

Notes and Suggestions.

1. The coloration alone in (*a*) is not a sufficient test for *phosphates*, since the molybdic solution produces a similar result with arsenic acid. The latter, however, gives no precipitate unless slightly warmed. *Arsenic* may be removed by precipitating with hydrogen sulphide in a hot acidulated solution.

2. The precipitate in (*a*) is soluble in excess of hydrochloric and phosphoric acids and in solutions of chlorides and phosphates, but is insoluble in the ammonium molybdate. A considerable excess of the latter is therefore desirable.

Experiment 45. — Boric Acid and Borates.

(*a*) The free acid may be recognized by mixing it with a little alcohol, and igniting, *a yellowish-green color being imparted to the flame.*

(*b*) Put a small quantity of borax, $Na_2B_4O_7$, into an evaporating dish, and moisten with strong sulphuric acid, which will set boric acid, H_3BO_3, free. Add sufficient alcohol to make a thin paste, and ignite. *The characteristic green flame proves the presence of a Borate.*

SUPPLEMENTARY. — 1. Take 1 cc. solution of borax, $Na_2B_4O_7$, and *barely* acidulate with hydrochloric acid. Moisten one end of a slip of turmeric paper with it and allow to dry. A characteristic red tint is imparted to the paper.

Notes and Suggestions.

1. Since copper salts also impart a green tint to a flame, it is necessary in practical analysis to exclude them before testing for *borates*. This may be done by precipitating them with hydrogen sulphide, filtering, and then boiling the filtrate to remove the excess of the reagent.

2. The test in (*b*) is unreliable in the presence of *chlorides*, since alcohol combines with them to form ethyl chloride, which also tinges *the flame green.*

3. If the substance to be tested is in the form of a solution, and requires concentration, it should be made alkaline before evaporating in order to prevent the escape of *boric acid.*

Experiment 46.—Oxalic Acid and Oxalates.

(*a*) Put into a test-tube a small quantity of oxalic acid, $C_2H_2O_4$, in the dry state (if in solution, carefully evaporate to dryness), add an excess of concentrated sulphuric acid, and heat. Carbon monoxide, CO, and carbon dioxide, CO_2, will escape with effervescence. The former may be kindled at the mouth of the test-tube, and the latter identified as in Experiment 48.

(*b*) Repeat (*a*), using ammonium oxalate, $(NH_4)_2C_2O_4$, instead of oxalic acid. The *simultaneous formation of carbon monoxide*, CO, and *carbon dioxide*, CO_2, *indicates the presence of an Oxalate.*

(*c*) To 5 cc. solution of ammonium oxalate add sufficient ammonium hydroxide to make alkaline, and then a small quantity of calcium sulphate solution. A white pulverulent precipitate of calcium oxalate, CaC_2O_4, is formed. Filter, wash, and digest the precipitate with acetic acid. The precipitate does not dissolve, *indicating the presence of an Oxalate.* [*Sulphate, Fluoride.*] To confirm the test, filter, wash, heat to *low redness*, and treat the residue with a few drops of acetic acid. An effervescence *proves the presence of an Oxalate in the original solution.*

Notes and Suggestions.

1. If the quantity of material operated upon in (*a*) is small, or if it should contain an admixture of a *carbonate* or other salt of a volatile acid, it may be found impossible to ignite the escaping carbon monoxide.

2. As was observed in Experiment 42, *oxalates* undergo decomposi*tion at a red heat*, carbon monoxide and carbon dioxide being evolved.

Carbonates, oxides, or pure metals are left behind, according to the temperature and the reducibility of the substance.

3. Since, in practical analysis, mixtures of other salts may be present that evolve carbonic oxide and carbon dioxide under the conditions indicated in (*a*), too much reliance must not be placed upon this test. The indication should be confirmed in every instance by the test in (*c*).

4. Instead of igniting the insoluble residue in (*c*), it is advised by some to dissolve it in dilute sulphuric acid, and add a few drops of solution of potassium permanganate, $KMnO_4$. Warm slightly. The decolorization of the permanganate proves the presence of an *oxalate*.

Experiment 47. — Hydrofluoric Acid and Fluorides.

(*a*) Put about 1 g. of finely pulverized calcium fluoride into a platinum crucible or a small lead cup, and mix with it sufficient concentrated sulphuric acid to make a thin paste. Cover with a watch-glass whose convex side has been coated with a thin layer of wax through which some lines have been traced by a sharp-pointed piece of wood. Fill the watch-glass with cold water to keep the wax from melting, and heat the crucible or cup gently in the hood for about half an hour, being careful to avoid inhaling the escaping gas or having it come in contact with the skin. Cautiously warm the watch-glass to soften the wax, and wipe it with a piece of paper. The tracing will be found etched into the glass.

$$CaF_2 + H_2SO_4 = 2\,HF + CaSO_4.$$

$$4\,HF + SiO_2 = SiF_4 + 2\,H_2O.$$

(*b*) Put a mixture of powdered calcium fluoride and fine dry sand into a short test-tube, add concentrated sulphuric acid, and heat. Suspend a drop of water in the mouth of the test-tube by means of the loop of a platinum wire. The water will become more or less cloudy or opaque, owing to *the setting* free of flocculent tufts of silica. *This proves the presence of a Fluoride.*

Notes and Suggestions.

1. The etching in (*a*) is due to the action of *hydrofluoric acid*, HF, which combines with the silica of the glass, forming silicon tetrafluoride, SiF_4, a gas.

2. On account of the presence of the silica in (*b*), silicon tetra-fluoride is evolved. This in combination with water forms silicic acid and hydrofluosilicic acid, H_2SiF_6.

3. It is evident that in testing for *fluorides*, the presence or absence of silica must be taken into consideration. If absent, test as in (*a*); if present, test as in (*b*), but omitting the addition of the sand.

4. Since there are some *fluorides* that are not decomposable by sulphuric acid, a negative result from the above tests is not conclusive. In such cases fusion with sodium carbonate is required to decompose the compound.

Experiment 48. — Carbonic Acid and Carbonates.

(*a*) Evaporate 5 cc. solution of sodium carbonate, Na_2CO_3, until saturated. Pour it into a test-tube, and add dilute hydrochloric acid. Brisk effervescence, without any special odor, *indicates a Carbonate.* Confirm by inclining the test-tube over another containing 5 cc. of lime water, so that the escaping gas will fall into the lime water. Cover the latter with the thumb, and shake. It becomes clouded, owing to the formation of calcium carbonate, $CaCO_3$.

(*b*) Repeat (*a*), using a small lump of limestone instead of sodium carbonate. Result?

Notes and Suggestions.

1. In testing a solid, as in (*b*), especially if it has an alkaline base, it is necessary to add the acid in excess in order to avoid the formation of an acid carbonate, which may prevent effervescence.

Experiment 49 — Silicic Acid and Silicates.

(*a*) Make a bead on a loop of platinum wire with micro-*cosmic salt,* $NaNH_4HPO_4$, dip into a solution of sodium

silicate, Na_2SiO_3, and heat intensely in the Bunsen flame. Small spicules of silica floating about undissolved on the bead *prove the presence of a Silicate.*

(*b*) Repeat (*a*), using finely powdered silica, SiO_2, instead of sodium silicate. Result?

(*c*) To 5 cc. solution of sodium silicate add dilute hydrochloric acid. *Silicic acid*, H_4SiO_4, will separate as a gelatinous precipitate. Evaporate to dryness, moisten with concentrated hydrochloric acid, and again evaporate to dryness. Silica will be left behind as a hard, gritty powder, insoluble in water or hydrochloric acid.

Notes and Suggestions.

1. In highly dilute solutions of *silicates*, or when added rapidly in excess, hydrochloric acid may fail to produce a precipitate; but if evaporated to dryness and ignited, *silica* will separate out and will not redissolve in hydrochloric acid.

2. There are but two *silicates* that are soluble in water, sodium silicate, Na_2SiO_3, and potassium silicate, K_2SiO_3. Other *silicates* may be made soluble by fusing them on platinum foil with a mixture of potassium and sodium carbonates.

Experiment 50. — Sulphurous Acid and Sulphites.

(*a*) Take 5 cc. solution of sodium sulphite, Na_2SO_3, in a test-tube. Add a small quantity of hydrochloric acid, and warm. Moisten a piece of filter paper with potassium dichromate, $K_2Cr_2O_7$, and hold in the mouth of the test-tube. *It will be turned green*, owing to the formation of chromium sulphate, $Cr_2(SO_4)_3$. The escaping sulphur dioxide, SO_2, may also be recognized by its odor.

(*b*) Repeat (*a*), using a small piece of calcium sulphite, $CaSO_3$, instead of sodium sulphite.

(*c*) To 5 cc. solution of sodium sulphite add a small *quantity of* barium chloride solution, $BaCl_2$. Barium sul-

phite, $BaSO_3$, is precipitated. Add sufficient dilute hydrochloric acid to dissolve the precipitate, and then a small quantity of chlorine water. A white precipitate is formed, barium sulphite being oxidized to barium sulphate. *This proves the presence of a Sulphite in the original solution.*

SUPPLEMENTARY. — 1. To 5 cc. solution of sodium sulphite add a small quantity of calcium chloride solution, $CaCl_2$. Calcium sulphite, $CaSO_3$, is partially precipitated.

2. To 5 cc. solution of sodium sulphite add a small quantity of solution of ferric chloride, $FeCl_3$. A red solution of ferric sulphite, $Fe_2(SO_3)_3$, is produced, or, in very concentrated solutions, a yellow precipitate of basic ferric sulphite. Heat. The solution is decolorized, ferrous sulphate being formed.

Notes and Suggestions.

1. While barium chloride precipitates normal *sulphites*, it does not precipitate free *sulphurous acid.*

2. In case *sulphates* should be present, they will be precipitated with the *sulphites* by barium chloride in (*c*). Upon digesting with hydrochloric acid, however, the barium sulphite goes into solution, while the barium sulphate is insoluble. By filtering, the separation is made complete. If now upon the addition of the chlorine water a precipitate forms, it is evident that a *sulphite* was present in the original solution.

Experiment 51. — Thiosulphuric Acid and Thiosulphates.

(*a*) Repeat Experiment 50 (*a*), using solution of sodium thiosulphate, $Na_2S_2O_3$, instead of sodium sulphite, Na_2SO_3. Sulphur dioxide is set free after a short time, as shown by the odor and by the effect upon potassium dichromate, $K_2Cr_2O_7$, and white or cream colored sulphur is precipitated. *This proves the presence of a Thiosulphate.*

SUPPLEMENTARY. — 1. To 5 cc. solution of sodium thiosulphate add a small quantity of solution of calcium chloride. No precipitate is formed.

2. To 5 cc. solution of sodium thiosulphate add a small quantity of

solution of ferric chloride, $FeCl_3$. A reddish-violet coloration is produced. Heat. The solution is decolorized, ferrous chloride being formed.

Notes and Suggestions.

1. The deportment of *sulphites* and *thiosulphates* toward reagents is so similar that considerable care is needed to distinguish between them. Hydrochloric acid causes an evolution of sulphur dioxide from both classes of compounds, but in the latter instance it is accompanied by the separation of sulphur. It should be borne in mind, however, that *sulphides* in the presence of oxidizing agents will also give a precipitate of sulphur upon the addition of an acid.

Experiment 52. — Sulphates, Sulphites, and Thiosulphates.

Remark. — In order to detect *Sulphates*, *Sulphites*, and *Thiosulphates* in mixtures containing two or more of the compounds, the following method of procedure is recommended: —

Procedure. — (*a*) To the solution add barium chloride and ammonium chloride in excess, and then dilute hydrochloric acid. The insolubility of a portion of the precipitate *proves the presence of a Sulphate.*

(*b*) Filter, add a few crystals of iodine to the filtrate, and heat to boiling. Barium sulphite is oxidized to barium sulphate, which is precipitated, *proving the presence of a Sulphite in the original solution.* The barium thiosulphate is oxidized to a tetrathionate.

(*c*) Filter, and treat the filtrate with bromine, oxidizing the soluble tetrathionate to the insoluble sulphate, *proving the presence of a Thiosulphate in the original solution.*

Experiment 53. — Arsenious Acid and Arsenites. Arsenic Acid and Arsenates.

Remark. — The presence of arsenic is determined by the test given in Experiment 9. Our only concern here is

to learn how to distinguish between an arsenite and an arsenate.

Procedure. — (*a*) Take 5 cc. solution of sodium arsenite, Na_3AsO_3. See that it is *neutral* or slightly alkaline with ammonium hydroxide, avoiding excess of the reagent. Add a few drops of silver nitrate solution. The formation of a yellow precipitate of silver arsenite, Ag_3AsO_3, readily soluble in dilute acids and ammonium hydroxide, *proves the presence of an Arsenite.*

(*b*) Repeat (*a*), using solution of sodium arsenate, Na_3AsO_4, instead of sodium arsenite, Na_3AsO_3. A light brown or reddish-brown precipitate of silver arsenate, Ag_3AsO_4, having the same solubilities as the arsenite, *shows the presence of an Arsenate.*

(*c*) To 5 cc. solution of sodium arsenite add a small quantity of magnesia mixture ($MgSO_4 + NH_4Cl + NH_4OH$). No precipitate is formed.

(*d*) Repeat (*c*), using sodium arsenate instead of sodium arsenite. A white crystalline precipitate of magnesium-ammonium arsenate, $MgNH_4AsO_4$, is formed.

(*e*) To 5 cc. solution containing both sodium arsenite and sodium arsenate add magnesia mixture to complete precipitation. What is the precipitate? Filter. To the filtrate add a few drops of silver nitrate solution? Result? To the residue on the filter paper add a drop of silver nitrate solution. Result?

(*f*) To 5 cc. solution of sodium arsenite add caustic soda in excess and then *a few drops* of a dilute solution of copper sulphate, $CuSO_4$. A clear blue liquid is obtained. Boil. A red precipitate of copper oxide, Cu_2O, is produced. This test is characteristic in the absence of copper salts or of organic matter.

(*g*) Repeat (*f*), using solution of sodium arsenate instead of sodium arsenite. Result?

(*h*) To 5 cc. solution of sodium arsenate add sufficient nitric acid to acidulate, and then a small quantity of ammonium molybdate. A yellow coloration results. Heat to 30° or 40°. A yellow precipitate is formed, and the liquid above the precipitate has a yellow color.

(*i*) Repeat (*h*), using sodium arsenite instead of sodium arsenate. Result?

Notes and Suggestions.

1. With such a variety of characteristic reactions at our disposal, but little difficulty need be experienced ordinarily in distinguishing between *arsenites* and *arsenates*. The circumstances must determine which tests are applicable.

2. In the presence of *phosphates* the test in (*d*) is unreliable, since they produce a similar precipitate with magnesia mixture.

3. Copper salts may interfere with the silver tests in (*a*) and (*b*) and will render unreliable the test in (*f*). If present, proceed as follows: —

To 5 cc. of the solution add an equal volume of a saturated solution of sodium carbonate, and boil at least fifteen minutes, replacing the water lost by evaporation. Copper carbonate, $CuCO_3$, is precipitated. Filter. Divide the filtrate into two portions. Acidulate the first portion with nitric acid, and add solution of silver nitrate. If a precipitate is formed [*chloride*, *bromide*, *iodide*, *cyanide*], filter it out, and to the filtrate add a few drops of ammonium hydroxide, letting it run down the sides of the test-tube so as to avoid mixing with the acid solution. A precipitate of arsenite or arsenate of silver [see (*a*) and (*b*)] will be formed as a thin film at the junction of the two liquids. To the second portion add caustic soda in excess, and test as in (*f*) and (*g*).

4. The similarity of the deportment of molybdate solution toward *arsenates* and *phosphates* was referred to in Experiment 44.

Experiment 54. — Chromic Acid and Chromates.

General Remarks. — The presence of *Chromium* is determined by the test given in Experiment 24. It may be

present as a base or as a chromate. If present as a base, no precipitates will be formed upon the addition of the group reagents, barium chloride or silver nitrate; if as a chromate, it will be precipitated by barium chloride in *neutral solutions*. The confirmatory test for *Chromium* is as follows: —

Procedure. — (*a*) Take 5 cc. solution of potassium chromate, K_2CrO_4, acidulate with acetic acid, and add a few drops of solution of lead acetate, $Pb(C_2H_3O_2)_2$. A bright yellow precipitate of lead chromate, $PbCrO_4$, *proves the presence of a Chromate.*

GROUP III (HYDROCHLORIC ACID GROUP).

HYDRIODIC, HYDROBROMIC, HYDROCHLORIC, HYDROCYANIC, NITROUS, AND HYDROSULPHURIC ACIDS.

Remark.—This group includes those acids which are precipitated in neutral solutions by silver nitrate, and not by barium chloride.

Experiment 55.—Hydriodic Acid and Iodides.

(*a*) Take 5 cc. solution of potassium iodide, KI, and concentrate by evaporation until saturated. Transfer to a test-tube, and put into it two or three small pieces of manganese dioxide, MnO_2. Add *just one drop* of dilute sulphuric acid, and heat. A violet vapor *indicates an Iodide.*

(*b*) To confirm the presence of iodine, put into the mouth of the test-tube a slip of paper upon which some thin starch paste has been spread. The blue coloration of the starch, due to the formation of iodized starch, *proves the presence of Iodine.*

(*c*) To 2 cc. solution of potassium iodide add a few drops of carbon disulphide, CS_2, and a drop or two of chlorine water. Shake, and then allow the carbon disulphide to subside. The iodine, freed by the action of the chlorine, is dissolved by the carbon disulphide, and forms a violet-colored solution. *This proves the presence of Iodides.*

(*d*) To 5 cc. solution of potassium iodide add a small *quantity* of a mixture of one part solution of copper sul-

phate, $CuSO_4$, and two and one-half parts solution of ferrous sulphate, $FeSO_4$. Cuprous iodide, CuI, is formed as a dirty white precipitate, *indicating the presence of an Iodide.*

(*e*) To 5 cc. of a saturated solution of potassium iodide add a few drops of concentrated sulphuric acid, and heat. A violet vapor *indicates an Iodide.*

SUPPLEMENTARY.—1. To 5 cc. solution of potassium iodide add two or three drops of thin starch paste, and stir until thoroughly mixed. Keep cold. Add a single drop of chlorine water. A blue tint results. To show the effect of an excess of chlorine, continue adding the chlorine water, drop by drop, until the blue coloration is discharged. The blue iodide of starch is decomposed, and the iodine oxidized to colorless iodic acid.

2. To 5 cc. solution of potassium iodide add two or three drops of thin starch paste. Mix. Slightly acidulate with dilute hydrochloric acid. Add a drop or two of a concentrated solution of potassium nitrite, KNO_2. Blue iodide of starch is formed. Heat. The color disappears. Cool. The color is restored.

3. To 5 cc. solution of potassium iodide add a few drops of solution of silver nitrate. Silver iodide is formed as a yellowish-white precipitate. Filter and wash. Digest with concentrated ammonium hydroxide. The precipitate is practically insoluble.

Experiment 56.—Hydrobromic Acid and Bromides.

(*a*) Take 5 cc. solution of potassium bromide, KBr, and concentrate by evaporation until saturated. Transfer to a test-tube, and put into it two or three small pieces of manganese dioxide, MnO_2. Add 2 or 3 cc. dilute sulphuric acid, and boil, at the same time holding in the mouth of the test-tube a slip of starch paper. The formation of a reddish-brown vapor which colors the starch yellow or orange-yellow *indicates a Bromide.*

(*b*) To 2 cc. solution of potassium bromide add a few drops of carbon disulphide, and then dilute chlorine water,

drop by drop. Shake, and allow the heavier liquid to subside. The *Bromine* is dissolved by the carbon disulphide, which acquires a yellowish or reddish-yellow tint, and settles to the bottom of the vessel. *This proves the presence of a Bromide.*

(*c*) To 5 cc. of a saturated solution of potassium bromide add a few drops of concentrated sulphuric acid, and heat. A reddish-brown vapor *indicates a Bromide.*

SUPPLEMENTARY. — 1. To 5 cc. solution of potassium bromide add one or two drops of chlorine water. A yellowish-red tint indicates free *bromine.* Continue adding chlorine water, drop by drop, to excess. Bromine chloride, $BrCl$, is formed, and the red coloration nearly or quite disappears.

2. To 5 cc. solution of potassium bromide add a small quantity of a mixture of one part copper sulphate solution and two and a half parts ferrous sulphate solution. No precipitate is formed.

3. To 5 cc. solution of potassium bromide add a few drops of solution of silver nitrate. A pale yellow precipitate of silver bromide, $AgBr$, is formed. Filter and wash. Digest with concentrated ammonium hydroxide. The precipitate is sparingly soluble.

Notes and Suggestions.

1. Excess of chlorine water must be avoided in (*b*), since it will combine with the *bromine* to form the colorless bromine chloride.

2. *Bromine* cannot be identified by the above tests in the presence of *iodides.* The latter may be eliminated by the method suggested in Experiment 58, or by the following treatment: To the mixture add carbon disulphide and dilute chlorine water as instructed in Experiment 55 (*c*). *Iodine* will be liberated, and will impart a violet to black color to the carbon disulphide. Continue adding chlorine water and carbon disulphide, and agitating, as long as the *iodine* tint seems to deepen. Separate the liquids by filtration through a wet filter. Repeat the operation, if necessary, until the *iodine* color is no longer obtained. Then continue the addition of chlorine water and carbon disulphide in the test for *bromine* as instructed in Experiment 56 (*b*).

Experiment 57. — Hydrochloric Acid and Chlorides.

(*a*) Take 5 cc. solution of sodium chloride, $NaCl$, and concentrate by evaporation until saturated. Transfer to a test-tube, and put into it two or three small pieces of manganese dioxide, MnO_2 (free from chlorides). Add 2 or 3 cc. strong sulphuric acid, and warm, at the same time holding in the mouth of the test-tube a strip of moist litmus paper. The formation of a yellowish-green gas, which readily bleaches the litmus paper, *proves the presence of a Chloride.*

(*b*) To 5 cc. solution of sodium chloride add a few drops of solution of silver nitrate. Silver chloride, $AgCl$, is precipitated. Filter and wash. Digest with concentrated ammonium hydroxide. The precipitate readily dissolves. Acidulate with nitric acid. The silver chloride is reprecipitated. *This indicates a Chloride.*

(*c*) Triturate about one-half gram of sodium chloride with an equal quantity of potassium dichromate, and put into a perfectly dry side-neck test-tube. Add 1 cc. of concentrated sulphuric acid. Close the mouth of the test-tube with a rubber stopper, and heat *gently*. The hydrochloric acid, formed through the action of the sulphuric acid on sodium chloride, combines with the potassium dichromate to form the volatile chromium dioxydichloride, CrO_2Cl_2, which rises as a bright brownish-red vapor. Let some of the gas pass into a test-tube containing 1 or 2 cc. of dilute ammonium hydroxide, and mix by shaking. Ammonium chromate, $(NH_4)_2CrO_4$, is formed as a yellow solution, *indicating Chlorides.*

$$CrO_2Cl_2 + 4\ NH_4OH = (NH_4)_2CrO_4 + 2\ NH_4Cl + 2\ H_2O.$$

To confirm the test, acidulate the solution with acetic acid, *and* add a few drops of lead acetate solution. The forma-

tion of a yellow precipitate (lead chromate) is *conclusive evidence of the presence of Chlorides in the original material.*

(*d*) To 5 cc. concentrated solution of sodium chloride in a test-tube add a few drops of concentrated sulphuric acid. A slight effervescence takes place, and *Hydrochloric acid*, HCl, having an irritating odor, is set free. Introduce a drop of ammonium hydroxide, suspended on the loop of a platinum wire or on a stirring-rod. *A white cloud is formed.*

SUPPLEMENTARY. — 1. To 5 cc. solution of sodium chloride add a small quantity of a mixture of one part copper sulphate and two and one-half parts ferrous sulphate. No precipitate is formed.

Notes and Suggestions.

1. In order to make a success of the test in (*c*), the apparatus and material employed must be perfectly dry, since the dioxydichloride is decomposed by water, forming chromic acid: —

$$CrO_2Cl_2 + 2\ H_2O = H_2CrO_4 + 2\ HCl.$$

If the substance under examination is in the form of a solution, it is necessary, therefore, to evaporate to dryness before making the test.

2. The presence of *bromides* does not interfere with the test in (*c*). Free *bromine* is released through the action of the sulphuric acid, but the compounds it forms with ammonium hydroxide are colorless.

3. *Iodides*, when present in considerable quantity, interfere with the test in (*c*), and they should be removed by the method advised in Experiment 58 *C* (*b*).

Experiment 58. — Hydriodic, Hydrobromic, and Hydrochloric Acids.

General Remarks. — The separation and determination of *Iodides*, *Bromides*, and *Chlorides* is somewhat tedious and troublesome, but with care and patience the results will prove highly satisfactory and conclusive. Three methods are here suggested, each of which has its ad-

vantages, and it is desirable that the student should be familiar with all of them.

Procedure.

A.

(*a*) Take 10 cc. solution containing potassium iodide, KI, potassium bromide, KBr, and sodium chloride, NaCl, and concentrate by evaporation until saturated.

(*b*) Transfer to a test-tube, and test for *Iodides* as in Experiment 55 (*a*) and (*b*). If found to be present, continue adding sulphuric acid, *a drop at a time*, and heating until violet vapor ceases to be given off.

(*c*) Then add 2 or 3 cc. dilute sulphuric acid, and test for *Bromides* as in Experiment 56 (*a*). Boil until bromine ceases to pass away, and cool the solution.

(*d*) Finally add 2 or 3 cc. strong sulphuric acid, and test for *Chlorides* as in Experiment 57 (*a*).

B.

(*a*) Take 10 cc. solution containing potassium iodide, potassium bromide, and sodium chloride, and concentrate by evaporation until saturated. Divide the solution into three parts.

(*b*) To the first portion add a few drops of carbon disulphide, CS_2, and one drop of chlorine water, and note indications of *Iodides*, as in Experiment 55 (*c*).

(*c*) To the second portion add a mixture of copper sulphate and ferrous sulphate to complete precipitation, as in Experiment 55 (*d*). Cuprous iodide, CuI, is precipitated. Filter, and test the filtrate for *Bromides* as in Experiment 56 (*b*).

(*d*) To the third portion add sufficient nitric acid to *acidulate* and then solution of silver nitrate, $AgNO_3$, to

complete precipitation. Silver iodide, AgI, silver bromide, AgBr, and silver chloride, AgCl, are precipitated. Filter and wash.

(*e*) Digest the precipitate from (*d*) in a strong hot solution of acid ammonium carbonate. Silver chloride will dissolve, silver bromide *very slightly*, while silver iodide is insoluble. Filter.

(*f*) Neutralize the filtrate from (*e*) with dilute nitric acid. Silver chloride is thrown down as a white precipitate, *indicating the presence of Chlorides.*

(*g*) To confirm the presence of *Chlorides*, fuse the precipitate from (*f*) with sodium carbonate on a piece of porcelain, dissolve the resulting sodium chloride in water, and test for *Chlorides* as in Experiment 57 (*a*).

C.

(*a*) Follow the instructions in *B*, proceeding as far as (*d*), proving the presence of *Iodides* and *Bromides*.

(*b*) To the third portion of the solution add about 2 grams of potassium dichromate dissolved in 5 cc. of water, evaporate to dryness, and fuse. The *Iodine* is completely liberated: $6\,KI + 5\,K_2Cr_2O_7 = 8\,K_2CrO_4 + Cr_2O_3 + 3\,I_2$.

Triturate the residue with an equal quantity of potassium dichromate, and test for *Chlorides* exactly as instructed in Experiment 57 (*c*).

Experiment 59. — Hydrocyanic Acid and Cyanides.

(*a*) To 5 cc. solution of potassium cyanide, KCN, add a few drops of caustic soda solution and 1 cc. or 2 cc. solution of ferrous sulphate. Digest warm for a few minutes, and then add a few drops of ferric chloride solution. A precipitate of ferrous and ferric hydroxides is thrown down. *Slightly* acidulate with dilute hydrochloric acid. The

hydroxides are dissolved and Prussian blue appears. *This proves the presence of Hydrocyanic acid.*

(*b*) To 5 cc. solution of potassium cyanide add a few drops of yellow ammonium sulphide, and evaporate on the water-bath to dryness. The residue contains ammonium thiocyanate, NH_4CNS, and potassium thiocyanate, KCNS. Dissolve it in a small quantity of dilute hydrochloric acid, and add a drop of ferric chloride solution. The formation of a blood-red solution of ferric thiocyanate, $Fe(CNS)_3$, *proves the presence of Cyanides in the original solution.*

(*c*) Take 5 cc. solution of potassium cyanide, and concentrate by evaporation. Place in the hood, and add a few drops of concentrated sulphuric acid. *Hydrocyanic acid*, HCN, a *quickly fatal poison*, is set free. Fan a little of the escaping gas toward the face, and notice the *peach-blossom odor.*

SUPPLEMENTARY. — 1. To 5 cc. solution of potassium cyanide add a small quantity of silver nitrate solution. A white precipitate of silver cyanide, AgCN, is thrown down. Filter and wash. Divide into two portions. To one add potassium cyanide solution in excess. The precipitate dissolves, forming the double cyanide of potassium and silver, $KAg(CN)_2$. To the other portion add ammonium hydroxide. The precipitate dissolves, though with some difficulty.

Notes and Suggestions.

1. Mercuric cyanide, $Hg(CN)_2$, cannot be detected by the above tests. If in the solid form, heat in a small test-tube under the hood. *Cyanogen* gas, C_2N_2, is set free, and may be recognized by the rose color imparted to a flame held near the mouth of the test-tube. If in solution, add hydrogen sulphide. Mercuric sulphide, HgS, precipitates, and the solution contains *hydrocyanic acid.* Filter, and test the filtrate for *cyanides* as in (*a*) and (*b*).

2. *Cyanogen* and *hydrocyanic acid* are *quick and violent poisons*, and the greatest precaution should at all times be exercised to avoid inhaling either gas, unless largely diluted with air. Ammonia and chlorine, by *inhalation*, are the antidotes.

Experiment 60.—Nitrous Acid and Nitrites.

(*a*) Take 5 cc. solution of potassium nitrite, KNO_2, in a test-tube, and mix with an equal volume of concentrated acetic acid, $HC_2H_3O_2$. Cautiously add a few drops of freshly prepared ferrous sulphate solution, letting it run down the sides of the test-tube so that the two liquids do not mix. Now lightly tap with the finger on the side of the test-tube. The formation of a dark brown ring where the liquids meet *proves the presence of Nitrous acid.*

(*b*) Repeat (*a*), using lead nitrite, $Pb(NO_2)_2$, instead of potassium nitrite, KNO_2. Result?

(*c*) To 2 cc. solution of potassium iodide, KI, add two or three drops of thin starch paste. Mix. *Slightly* acidulate with dilute sulphuric acid. Add a drop or two of solution of potassium nitrite. The nitrous acid, HNO_2, and hydriodic acid, HI, simultaneously formed through the action of the sulphuric acid, react upon each other according to the following equation: $HNO_2 + HI = I + H_2O + NO$. Blue iodide of starch is formed. *This proves the presence of Nitrites.*

(*d*) To 5 cc. solution of potassium nitrite add a small quantity of dilute sulphuric acid. Nitric oxide, NO, is evolved, and uniting with the oxygen of the air, gives brownish-red fumes of nitrogen peroxide, NO_2.

SUPPLEMENTARY.—1. To 1 cc. solution of potassium permanganate, $KMnO_4$, acidulated with sulphuric acid, add solution of potassium nitrite, drop by drop, to excess. The potassium permanganate is decolorized.

Notes and Suggestions.

1. *Nitrites* may act as oxidizing or reducing agents according to their relations. In (*a*) and (*b*) they play the former rôle, and in Supplementary Experiment 1, the latter. To understand the reaction in (*a*), see Experiment 63 (*b*).

2. Instead of the method suggested in (*a*), the following procedure is preferred by some analysts: Mix 5 cc. solution of potassium nitrite with an equal volume of concentrated acetic acid, and pour into a test-tube containing a crystal of ferrous sulphate. A dark brown cloud will soon appear above the crystal, proving the presence of a *nitrite.*

3. In the presence of *chlorates*, the test in (*a*) is unreliable.

Experiment 61.—Hydrosulphuric Acid and Sulphides.

(*a*) Take 5 cc. solution of sodium sulphide, Na_2S, in a test-tube. Add a small quantity of hydrochloric acid. Moisten a piece of filter paper with lead acetate and hold it in the mouth of the test-tube. *It will be stained black*, owing to the formation of lead sulphide, PbS. The escaping hydrogen sulphide will also be recognized by its disagreeable odor.

(*b*) Repeat (*a*), using a small piece of ferrous sulphide, FeS, instead of sodium sulphide, Na_2S. Result?

(*c*) To 5 cc. solution of sodium sulphide add a few drops of caustic soda solution and then a drop or two of solution of sodium nitro-prusside, $Na_2FeNO(CN)_5$. A rich purple coloration results, even in very dilute solutions, but disappears in a short time. *This proves the presence of Sulphides.*

(*d*) Fuse a small quantity of lead sulphide, PbS, with about half its bulk of sodium carbonate, in a porcelain crucible. Soluble sodium sulphide is obtained. Crush a portion of the product in a drop of water on a bright silver coin. A brownish-black stain upon the silver *proves the presence of a Sulphide.*

Notes and Suggestions.

1. In the presence of oxidizing agents, as *chlorates*, *chromates*, etc., *the test* described in (*a*) will fail, as hydrogen sulphide will not be *liberated*; sulphur is separated instead.

2. The test in (*c*) is applicable to the soluble metallic *sulphides* without the addition of the caustic soda, but since the free acid does not give the reaction, the presence of an alkali should be insured.

3. The test in (*d*) is applicable to all *sulphides* except in the presence of *sulphites* and *thiosulphates*, but is especially useful in the examination of those *sulphides* which are insoluble in water and which are undecomposed by hydrochloric acid.

4. In case the *sulphide* used in (*a*) is one that is not decomposed by hydrochloric acid, add a little powdered zinc. The compound will be reduced, with evolution of hydrogen sulphide. *Sulphites*, *thiosulphates*, and some *sulphates* may likewise be reduced.

Experiment 62. — Third Group Mixture.

General Remarks. — Since in a number of instances the tests for third group acids in each other's presence are unsatisfactory, the following plan of partial elimination is advised: —

Procedure. — (*a*) Take 10 cc. solution containing potassium iodide, potassium bromide, sodium chloride, potassium cyanide, potassium nitrite, and sodium sulphide. Add solution of zinc nitrate in excess. *Sulphides* and *Cyanides* are precipitated as zinc salts. Filter and wash.

(*b*) To the precipitate from (*a*) add sufficient dilute hydrochloric acid to dissolve. Test the escaping gas for *Sulphides* as in Experiment 61 (*a*), being careful to avoid inhaling the *Hydrocyanic acid* which is liberated simultaneously. When effervescence ceases, test the liquid for *Cyanides* as in Experiment 59 (*a*) and (*b*).

(*c*) Divide the filtrate from (*a*) into two parts. Test one portion for *Nitrites* as in Experiment 60 (*a*). To the other portion add solution of silver nitrate. *Iodides*, *Bromides*, *Chlorides*, and *Nitrites* are precipitated as silver salts. Acidulate with dilute nitric acid. The silver nitrite dissolves. Filter and wash, rejecting the filtrate.

(*d*) Divide the residue from (*c*) into two parts. Treat and test the first portion for *Chlorides* as in Experiment 58 *B* (*e*), (*f*), (*g*). Fuse the second portion with sodium carbonate in a porcelain crucible, and boil the fused mass with water. Iodide, bromide, and chloride of sodium go into solution, and should be tested for *Iodides* and *Bromides* as in Experiment 58 *B* (*a*), (*b*), (*c*).

GROUP IV (NITRIC ACID GROUP).

NITRIC AND CHLORIC ACIDS.

Remark. — This group includes those acids which are not precipitated by silver nitrate or barium chloride.

Experiment 63. — Nitric Acid and Nitrates.

(*a*) Take 5 cc. solution of potassium nitrate, KNO_3, in a test-tube, and treat it as was done with the potassium nitrite, KNO_2, in Experiment 60, substituting sulphuric acid for acetic acid. The formation of a brown ring *indicates the presence of Nitric acid.*

(*b*) Repeat (*a*), using dilute nitric acid instead of potassium nitrate, and omitting the sulphuric acid. Result?

The equations for the peculiar reactions indicated above are: —

$$2\,KNO_3 + 6\,FeSO_4 + 4\,H_2SO_4 = K_2SO_4 + 4\,H_2O + 2\,NO + 3\,Fe_2(SO_4)_3.$$

$$2\,FeSO_4 + NO = (FeSO_4)_2NO. \quad \text{(Brown ring.)}$$

(*c*) Into 5 cc. dilute nitric acid in an evaporating dish put a white quill cutting. Evaporate gently to dryness. The yellow coloration of the quill *shows the presence of free Nitric acid.*

(*d*) To 5 cc. concentrated solution of potassium nitrate add a few drops of concentrated sulphuric acid, and heat. Reddish-brown fumes of nitrogen peroxide are formed, *indicating a Nitrate.* To insure the test with most nitrates, a reducing agent (*e.g.* copper) should be present.

(*e*) To 5 cc. solution of potassium nitrate add a small piece of zinc amalgam or a few grains of finely divided zinc, and heat gently for some time. Potassium nitrate is reduced to potassium nitrite. Filter. Test the filtrate for nitrites as in Experiment 60 (*a*). *This is a positive test for Nitrates*, in the absence of nitrites in the original solution.

SUPPLEMENTARY. — 1. Evaporate 5 cc. solution of lead nitrate until saturated. Add a bit of copper turnings and then a few drops of concentrated sulphuric acid. Brownish-red fumes of nitrogen peroxide are given off.

2. Evaporate 5 cc. solution of potassium nitrate to dryness, being careful to avoid decomposition. To the residue add a *drop* of a mixture consisting of one part carbolic acid, C_6H_5OH, four parts strong sulphuric acid, and two parts water. Nitro-compounds, of a deep reddish-brown color, are formed. Add a drop of strong ammonium hydroxide. The color becomes yellow.

Notes and Suggestions.

1. The reaction in (*a*) must take place in the cold, since heat prevents the formation of the brown ring. After mixing the potassium nitrate and sulphuric acid, therefore, be careful to cool the solution before adding the ferrous sulphate. In connection with this test, read Note 2, Experiment 60.

2. The test in (*a*) is unreliable in the presence of *iodides* and *bromides*. They should first be removed by precipitation with silver sulphate, in a solution slightly acidulated with sulphuric acid.

3. The presence of *chlorates* and *chromates* interferes more or less with the test for *nitrates* in (*a*). *Chlorates* may be destroyed by mixing with sodium carbonate in excess, evaporating, and igniting *gently* for some time. The *chlorates* are converted into *chlorides*. To remove *chromates*, heat with a little dilute sulphuric acid and alcohol, thus bringing about a reduction of the chromic acid, and then add ammonium hydroxide to precipitate the chromium as chromium hydroxide, $Cr(OH)_3$.

4. None of the tests given for *nitrates* are reliable in the presence of *nitrites*. *Nitrites* may be destroyed by adding a little acetic acid to the solution, and heating. The residual solution may then be tested for *nitrates* as in (*a*), (*d*), and (*e*).

Experiment 64. — Chloric Acid and Chlorates.

(*a*) Evaporate 5 cc. solution of potassium chlorate, $KClO_3$, to dryness. Ignite. Potassium chlorate is decomposed into potassium chloride, KCl, and oxygen. Dissolve in the least necessary quantity of water, and test for *Chlorides* with a few drops of silver nitrate. White silver chloride, AgCl, is precipitated. *This is a test for Chlorates* in the absence or after the removal of *Chlorides.*

(*b*) Evaporate 5 cc. solution of potassium chlorate until saturated. *Cautiously* add a *few drops* of concentrated sulphuric acid, and heat *gently*. An offensive greenish yellow gas, consisting of a mixture of chlorine and chlorine dioxide, ClO_2, is given off with *explosive* violence.

(*c*) Repeat (*b*), using hydrochloric acid instead of sulphuric acid. A similar product is formed, but with less violence.

(*d*) To 5 cc. solution of potassium chlorate in a test-tube add sufficient indigo to color light blue. Acidulate with a few drops of dilute sulphuric acid. Cautiously drop into the blue fluid some sodium sulphite solution, Na_2SO_3. The indigo will be immediately decolorized, even *in the cold.*

Notes and Suggestions.

1. The test in (*b*) is a conclusive one in the absence of *hypochlorites* or *chlorides*, although in the latter case chlorine is set free only in the presence of an oxidizing agent.

2. The decolorization of the indigo solution in (*d*) is a phenomenon that belongs to *nitrates* as well as to *chlorates.* In the former case, *heat* must be applied; in the latter, it takes place in the *cold.* There are other substances, also, that decolorize, chiefly those from which chlorine is easily liberated.

3. In case *chlorides* are present, they must be removed before applying the test in (*a*). This may be done by adding silver nitrate solution to complete precipitation, and filtering. Treat the filtrate as in (*a*).

GROUP V (ORGANIC ACIDS).

TARTARIC AND ACETIC ACIDS.

Remark. — This group includes those acids whose salts are charred by heating.

Experiment 65. — Tartaric Acid and Tartrates.

(*a*) To 5 cc. solution of potassium sodium tartrate, $KNaC_4H_4O_6$, add about 1 cc. concentrated sulphuric acid, and heat. The mixture will darken rapidly, owing to the separation of carbon, while sulphur dioxide, carbon monoxide, and carbon dioxide will be evolved, accompanied by the odor of burnt sugar. *This indicates the presence of Tartaric acid.*

(*b*) Evaporate 5 cc. solution of potassium sodium tartrate until saturated. Add an excess of potassium acetate, $KC_2H_3O_2$, dissolved in alcohol, and a few drops of acetic acid. Add an equal volume of alcohol, shake, rub the sides of the vessel with a glass rod, and allow to stand for some time. The formation of a crystalline precipitate of hydrogen potassium tartrate, $HKC_4H_4O_6$, often adhering to the sides of the vessel, *proves the presence of a Tartrate* in the absence of other than sixth group metals.

(*c*) To 5 cc. solution of potassium sodium tartrate add solution of calcium chloride, $CaCl_2$, *in excess*. A white precipitate of calcium tartrate, $CaC_4H_4O_6$, is thrown down. *If slow in* forming, agitate the liquid and rub the sides of *the vessel* with a glass rod. Wash three or four times by

decantation, drain off the water as completely as possible, and add two or three drops of a solution of ammonium silver oxide, made by adding a *very slight* excess of ammonium hydroxide to silver nitrate solution. Heat the mixture gradually. A lustrous mirror of metallic silver will deposit on the sides of the test-tube.

SUPPLEMENTARY. — 1. Evaporate 5 cc. solution of potassium sodium tartrate to dryness, and heat to redness for a few minutes. The substance will darken in color and evolve the odor of burnt sugar.

2. To 5 cc. solution of potassium sodium tartrate add calcium hydroxide in excess. Calcium tartrate is formed as a white flocculent precipitate, subsequently assuming a crystalline form. Add sufficient caustic potash to dissolve the precipitate in the cold. Boil. The salt is thrown down as a gelatinous precipitate. Cool. It redissolves.

Experiment 66. — Acetic Acid and Acetates.

(*a*) The free acid may be recognized by its vinegar odor.

(*b*) To 5 cc. concentrated solution of ammonium acetate, $NH_4C_2H_3O_2$, add a small quantity of sulphuric acid and a little alcohol. Warm gently. Ethyl acetate, $C_2H_5(C_2H_3O_2)$, is formed, and *may be recognized by its highly characteristic and fragrant odor.*

SUPPLEMENTARY. — 1. Evaporate 5 cc. solution of sodium acetate to dryness, and heat to redness for a few minutes. The substance blackens, and inflammable vapor of acetone, C_3H_6O, passes off.

2. To 5 cc. neutral solution of sodium acetate, $NaC_2H_3O_2$, add one drop of ferric chloride solution. A deep red coloration is produced, owing to the formation of ferric acetate, $Fe(C_2H_3O_2)_3$. Boil. The iron is precipitated as a brownish-red basic acetate, and the fluid becomes colorless.

Experiment 67. — Detection of Acids in Complex Solutions and Soluble Mixtures.

***General* Remarks.** — The presence of one acid will *usually* not interfere with the test for others, so that

different acids may be successfully tested for in complex mixtures by working upon separate portions of the original substance.

As a rule, it is advisable to remove the non-alkaline metals from the solution before testing it for acids, since many metals give precipitates with the reagents employed, and, if present, might lead to false indications.

The determination of the bases should always precede that of the acids, as a knowledge of the metals present enables one to exclude such classes of salts as could not exist in solution with those metals. For example, if the substance under examination is soluble in water, and contains silver, it is obviously unnecessary to look for chlorides; or if barium is present in a neutral solution, it is at once inferred that sulphates, phosphates, carbonates, oxalates, and tartrates are absent, since these barium salts are all insoluble in water. It will be found helpful in this connection to consider the following partial summary from the Table of Solubilities: —

1. All normal chlorides, bromides, and iodides, except those of the first group metals and cuprous and mercuric iodides, are soluble in water.
2. All sulphates, except those of barium, calcium, strontium, and lead, and all nitrates, chlorates, and acetates, except some basic nitrates and acetates, are soluble in water.
3. All phosphates, borates, oxalates, carbonates, arsenites, and arsenates, except those of the alkali metals and chromium and stannic oxalates, are insoluble or but slightly soluble in water.
4. All salts of potassium, sodium, and ammonium, except the platini-chlorides of potassium and ammonium, are soluble in water.

The presence of chromates, arsenites, and arsenates is revealed in the basic analysis, since they are reduced by hydrogen sulphide in the presence of hydrochloric acid.

A careful regard for these preliminary examinations and inferences will greatly facilitate the determination of the acids, and compensate largely for the lack of systematic elimination and analysis.

Procedure.

A.

(*a*) Concentrate by evaporation 20 cc. of a solution containing representative acids of the several groups. Test with litmus paper. Ascertain what bases are present, either by analysis, or, if permissible, by inquiry of the instructor. Determine by consultation of the Table of Solubilities what classes of salts must be absent under the existing conditions.

(*b*) To a portion of the solution from (*a*) add dilute hydrochloric acid, in the cold, and look for indications of *Sulphites*, *Thiosulphates*, *Cyanides*, *Nitrites*, *Carbonates*, *Silicates*, *Sulphides*, and *Chlorates*, as given under the special tests for those salts. Heat the solution, and repeat the observations.

(*c*) To a second portion of the solution from (*a*) add a small quantity of concentrated sulphuric acid, and heat gently. Repeat the observations mentioned in (*b*), and look also for indications of *Fluorides*, *Nitrates*, *Acetates*, *Oxalates*, *Tartrates*, *Iodides*, *Bromides*, and *Chlorides*, as described in the special tests for those salts.

(*d*) If the original solution is neutral and free from non-alkaline metals, continue the examination for acids as in *B*. If it is not neutral, but is free from non-alkaline metals, neutralize it by the careful addition of ammonium

hydroxide, or of nitric acid, as may be necessary, and proceed as in *B*.

(*e*) In case other metals than sodium, potassium, and ammonium are present in the original solution, it is advisable to remove them before continuing the analysis. In the absence of *Arsenic* or *Antimony*, this is done most satisfactorily by adding to a portion of the original solution a *slight excess* of sodium carbonate, and boiling for some time, when the bases will be precipitated. Filter, and add to the filtrate dilute nitric acid, drop by drop, until *neutral*. Boil until no more carbon dioxide escapes, and test once more with litmus paper. Divide the solution into several parts and examine as directed in *B*, remembering that *Nitrates* and *Carbonates* must now be looked for in the original solution. If a precipitate forms upon neutralizing with nitric acid, it is probably silica or aluminum hydroxide, and should be filtered off and tested for *Silica* as in Experiment 49 (*a*). If *Arsenic* or *Antimony* is present, however, add hydrogen sulphide in excess to a portion of the solution, acidulating it if necessary, heat for some time, filter, and finally remove the excess of the reagent from the filtrate by boiling. Divide into several portions, and treat as in *B*. It must not be forgotten, however, that *Sulphides*, *Arsenites*, *Arsenates*, *Chlorates*, and *Chromates* should not be looked for in this filtrate, but must be sought in the original solution; also, that if *Chlorates* are present, the tests for *Chlorides* and *Sulphates* are rendered valueless, owing to oxidation of the hydrogen sulphide.

B.

(*a*) To a portion of the neutral solution, free from non-*alkaline* metals, add a small quantity of barium chloride (or *nitrate*). A precipitate may be any one or all of the acids

of the first and second groups. Add dilute hydrochloric acid to decidedly acid reaction. If a residue remains, *Sulphates* are present. If it wholly dissolves, the precipitate consisted of members of the second group, which should now be tested for individually, by working upon separate portions of the original solution or of the solution from which non-alkaline metals have been eliminated.

1. Test for *Phosphates* as in Experiment 44 (*a*).
2. Test for *Borates* as in Experiment 45 (*b*).
3. Test for *Oxalates* as in Experiment 46 (*c*).
4. Evaporate a portion of the solution to dryness, and test for *Fluorides* as in Experiment 47 (*a*).
5. Test some of the original solution for *Carbonates* as in Experiment 48 (*a*).
6. If *Silicates* were not revealed by the preliminary examination, test for them as in Experiment 49 (*a*) and (*c*).
7. Test for *Sulphites* and *Thiosulphates* as in Experiment 52, reviewing first the Notes and Suggestions in connection with Experiments 50 and 51.

(*b*) To another portion of the *perfectly neutral* solution, free from non-alkaline metals, add a small quantity of silver nitrate. A precipitate may consist of both second and third group acids. To the precipitate add cold dilute nitric acid. A precipitate remaining undissolved shows the presence of third group acids, which should be tested for individually in separate portions of the solution.

1. Test for *Iodides*, *Bromides*, and *Chlorides* as in Experiment 58, *B*.
2. Test for *Cyanides* as in Experiment 59 (*a*) and (*b*).
3. Test for *Nitrites* by Experiment 60 (*a*) and (*c*).
4. *If Sulphides* are present, they will probably have been revealed by the preliminary examination. Con-

firm, if necessary, by the test in Experiment 61 (*c*) and (*d*).

(*c*) As there is no general reagent for the acids of the fourth group, the members of this group must be sought for individually.

1. Test a portion of the original solution for *Nitrates*, as in Experiment 63 (*a*) and (*e*), giving careful attention to the Notes and Suggestions.
2. Test for *Chlorates* as in Experiment 64 (*a*), observing the precautions mentioned under the Notes and Suggestions.

(*d*) Evaporate a small portion of the original solution to dryness, and then heat to redness. If there is charring, organic acids or other organic bodies are present, and they may be identified by special tests.

1. Test for *Tartrates* as in Experiment 65 (*b*) and (*c*).
2. Test for *Acetates* as in Experiment 66 (*b*).

C.

If the foregoing tests for acids fail to reveal any of the classes of salts mentioned in this manual, the substance may be an oxide or hydroxide or a salt of some of the less common acids.

Notes and Suggestions.

1. If ammonium salts are present in considerable quantity in the original solution, or if much ammonia was added in *A* (*d*) for the purpose of neutralizing, the barium test for second group acids in *B* (*a*) is not strictly reliable, since most barium salts of this group are somewhat soluble in water containing ammonium salts. In this event, the presence or absence of members of this group must be determined by individual tests, as in *B* (*a*), 1–7.

2. Some helpful inferences may be drawn from the appearance of the insoluble residue in *B* (*b*). If blackish, a *sulphide* is probably *present; if* white, *sulphides* are absent, and *chlorides*, *bromides* or *cyanides* present; if yellowish, an *iodide* is indicated.

3. The indications in *B* (*b*) are of no value with respect to the determination of *nitrites*, since silver nitrite is soluble in nitric acid. They should be sought for, therefore, independently.

4. In case *sulphides* or *cyanides* are present, it will be best to use the method of separation and determination of third group acids recommended in Experiment 62.

5. In connection with the statement on p. 196 concerning the solubility of *chlorides*, it should be noted that the normal chlorides of *antimony*, *bismuth*, and *tin*, with the exception of stannic chloride, are rather easily decomposed by water, being changed into insoluble basic salts. The presence of free acid is required to keep them in solution.

PART III.

THE SYSTEMATIC EXAMINATION OF SUBSTANCES OF UNKNOWN COMPOSITION.

General Remarks. — The complete examination of a substance involves several distinct steps or operations whose orderly observance will greatly facilitate the work of analysis. It embraces both dry and wet processes, the former being included under what is known as the Preliminary Examination. While the examination in the dry way should never be omitted, its indications should seldom be accepted by the beginner as conclusive proof, without the confirmation of a wet analysis.

The body under examination may be a solid or a liquid. If a solid, it may be a pure metal or an alloy or some non-metallic solid; if a liquid, it may or may not contain solid matter in solution. Our method of procedure will be based upon these differences.

Since several portions of the material will be needed for a complete analysis, the supply should be husbanded with care, always reserving a small quantity for unforeseen contingencies.

SECTION I.

THE SUBSTANCE IS A SOLID.

I. It is a Metal or an Alloy.

Proceed as directed in Experiment 41.

II. The substance is a Salt, Mineral, or some other Non-metallic Solid.

A. PRELIMINARY EXAMINATION.

Examine the substance carefully with respect to its physical properties, noting the color, odor, specific gravity, hardness, crystalline form, etc. Reduce a portion of it to a fine powder in an agate or porcelain mortar, and subject to the following tests: —

THE CLOSED TUBE TEST.

aa. Introduce a little of the substance into a matrass or a dry glass tube, closed at one end. Wipe out the upper part of the tube with a twisted piece of tissue paper or a tuft of cotton on a wire. Apply heat, at first gentle, gradually raising to redness.

- **a.** Water is given off. It may be due to the presence of water of crystallization, to a hydroxide, or to water mechanically enclosed. In the latter event, its expulsion is usually accompanied by decrepitation. Test the expelled water with litmus paper. If alkaline, an ammonium salt is indicated. If acid, it points to the presence of some volatile acid, as hydrochloric, nitric, sulphuric, etc.
- **b.** A gas or vapor escapes.
  - (*a*) The gas is colorless and odorless.
    1. *Oxygen*, recognized by the glowing of a bit of coal placed on the heated substance. It indicates the presence of *Chlorates*, *Nitrates*, or *Peroxides.*
    2. *Carbon dioxide*, recognized by the turbidity produced in a drop of lime water. It shows the presence of *Carbonates* or *Oxalates*.
    3. *Carbon monoxide*, which burns with a blue flame. It indicates an *Oxalate* or occasionally a *Tartrate* or other *Organic* substance.
  - (*b*) The gas is colorless, with odor.
    1. *Ammonia*, recognized by its odor and effect upon litmus paper. It shows the decomposition of *Ammonium* compounds.
    2. *Sulphur dioxide*, recognized by its odor and bleaching effect on litmus paper. It indicates *Sulphites*, *Thiosulphates*, and occasionally *Sulphates*.
    3. *Acetone*, known by its characteristic fragrant odor. It indicates an *Acetate*.

    4. *Sulphuretted hydrogen*, recognized by its odor and blackening effect on paper moistened with lead acetate solution. It indicates the presence of a hydrated *Sulphide* or a *Sulphite*, or other *Sulphur*-containing body.
    5. *Cyanogen*, recognized by its characteristic odor and violet flame. *It is intensely poisonous.*
  - (*c*) The gas has color and odor.
    1. *Nitrogen peroxide*, recognized by its orange-red color and acrid odor. It indicates the presence of *Nitrates* or *Nitrites*.
    2. *Iodine*, known by its violet vapor and peculiar odor. It indicates *Iodides*.
    3. *Bromine*, recognized by its orange-colored fumes and pungent odor. It indicates *Bromides*.
    4. *Chlorine*, indicated by greenish-yellow fumes and peculiar odor. It shows the presence of *Chlorides*.
    5. *Organic bodies*. Some *Organic* substances give off brown or black vapors and an odor like burnt sugar or of ammonia.

c. A sublimate is formed.
  - (*a*) The sublimate is white.
    1. *Arsenic trioxide*. It consists of octahedral crystals.
    2. *Antimony trioxide*. It melts and then sublimes in needle-shaped crystals.
    3. *Mercurous chloride*. It sublimes without previous fusion. The sublimate is yellow while hot, white when cold.
    4. *Mercuric chloride*. It melts and then forms a crystalline sublimate.
    5. *Ammonium salts*. May be confirmed by removing sublimate, adding a drop or two of caustic potash, and heating.
  - (*b*) The sublimate is colored.
    1. *Arsenic*, recognized by the metallic mirror and garlic odor.
    2. *Mercury*, amalgam, and some of its compounds. A gray sublimate is formed, consisting of minute globules, which by friction may be made to unite.
    3. *Sulphur*. The sublimate consists of reddish-brown drops when hot, but pure yellow when cold. It indicates free *Sulphur*, a *Sulphide*, or a Thiosulphate.

4. *Iodine*. The sublimate is steel-gray.
5. *Antimonious sulphide*. It fuses yellow, and forms a white, amorphous sublimate.
6. *Antimonic sulphide*. The sublimation requires a high temperature. The sublimate is nearly black while hot, but reddish-brown when cold.
7. *Arsenious sulphide*. The sublimate is nearly black when hot, but reddish-yellow to yellow when cold.
8. *Mercury sulphide*. The sublimate is black and lustreless, but turns red on being rubbed.

d. The substance changes without volatilization.

(*a*) The substance changes color.

1. *Organic compounds*. They are blackened with the separation of carbon, and a characteristic odor is evolved. Tarry drops may sometimes condense in the upper part of the tube.
2. *Copper* and *Cobalt* salts. Many of these blacken at a high temperature.
3. *Zinc oxide* and most *Zinc* salts are yellow while hot, white when cold.
4. *Tin oxide* is yellowish brown when hot, light yellow when cold.
5. *Bismuth oxide* and many *Bismuth* salts are orange while hot, lemon-yellow when cold.
6. *Ferric oxide* and salts are red to black while hot, reddish brown when cold.
7. *Lead oxide* and *Lead* salts are yellow when hot or cold.
8. *Cadmium hydroxide* and many *Cadmium* salts are brown when hot or cold.

(*b*) The substance fuses.

1. This is true of many salts, but especially characterizes those of the *Alkali* metals.

e. The substance suffers no change. This indicates the absence of volatile bodies and of *Organic compounds*.

THE OPEN TUBE TEST.

bb. Introduce a small portion of the substance into a glass tube, open at both ends and three inches long, so that it will lie about one inch from the end. Incline the tube slightly, and apply a gentle heat at first, increasing it as may seem necessary. Many substances that undergo no change in the matrass are oxidized by this operation, and yield sublimates or gaseous products.

a. *Sulphur dioxide*, recognized by its odor and action on moistened blue litmus paper. This indicates the presence of free *Sulphur*, *Sulphides*, or *Thiosulphates*.

b. *Arsenic trioxide*, recognized by the white sublimate of minute octahedral crystals.

c. *Mercury* and amalgams, recognized by the gray sublimate of minute globules.

d. *Antimony oxides*, recognized by the white fumes which partly escape and partly condense in the tube.

e. *Bismuth oxide*. It sublimes as brownish globules while hot, becoming pale yellow when cold.

f. *Tellurium dioxide*. It is formed as a gray sublimate in the upper part of the tube.

g. *Selenium oxide*, recognized by the odor resembling that of rotten horse-radish.

THE REDUCTION TEST.

cc. Mix a quantity of the powdered substance equivalent in bulk to a hemp seed with an equal bulk of sodium carbonate, and rub to a paste with a small drop of water. Make a small cavity about the size of half a pea in that side of a piece of charcoal showing the annular rings. Place the paste in the cavity, hold the charcoal horizontally, and expose the assay to the *reducing-flame* of the blow-pipe for several minutes. Some substances unite with soda to form fusible compounds, some form infusible compounds, and others are not acted upon at all. Many metallic oxides are reduced to metals, forming beads or incrustations which may be identified. At the close of the operation, if a single large globule has not been obtained, the fused mass and the charcoal about it should be cut out and ground up with water in an agate or porcelain mortar. The lighter portions of the assay and the particles of charcoal may then be washed away by successive additions of water. The metal will remain in the mortar as a dark heavy powder or as flattened scales or spangles, which should be examined with the magnifying-glass and also with the magnet.

a. A metallic globule is formed.
  - (*a*) *Lead*, recognized by its easy fusibility and malleability. A yellow incrustation is simultaneously formed on the charcoal.
  - (*b*) *Copper*, identified by the red, malleable metallic globules or spangles.
  - (*c*) *Gold*, recognized by the yellow, malleable globule, produced without incrustation.
  - (*d*) *Tin*, formed as a white, malleable bead, with a slight incrustation, which is yellow while hot, white when cold.
  - (*e*) *Silver*, recognized by the white, brilliant, malleable globule which is produced without incrustation.
  - (*f*) *Bismuth*, formed as a gray or reddish-white brittle bead, with an orange incrustation while hot, lemon-yellow when cold.
  - (*g*) *Antimony*, formed as a white brittle bead with a white incrustation.

b. An incrustation is formed, but the substance does not fuse to a bead.
  - (*a*) *Cadmium*, recognized by the reddish-brown coating with a variegated border. In thin layers it is orange-yellow.
  - (*b*) *Arsenic*, identified by the white, volatile incrustation formed at some distance from the assay, and the garlic-like odor evolved.
  - (*c*) *Zinc*, formed as a yellow incrustation in close proximity to the assay. It turns white on cooling, and is volatilized with great difficulty. Upon moistening with solution of cobalt nitrate, and igniting strongly, the mass becomes yellowish-green when cool.
  - (*d*) *Sulphur*. This is liable to pass away as a vapor, and may be recognized by the odor of sulphur dioxide, but in part may deposit as a yellow incrustation at some distance from the assay.

c. A fusible mass is obtained, but no bead.
  - (*a*) *Chromium* compounds, formed as a yellow mass.
  - (*b*) *Manganese* compounds, formed as a green mass.

d. An infusible, magnetic powder is obtained. This may consist of oxides of *Iron*, *Nickel*, or *Cobalt*.

e. Unclassified phenomena.
  - (*a*) *Silica*, recognized by the transparent glassy bead, which remains transparent upon cooling if soda is not in excess.

(*b*) *Lime*, *Magnesia*, *Alumina*. These substances are not attacked by the soda, but remain unchanged while the soda sinks into the charcoal.

(*c*) *Barium* and *Strontium* salts form fusible compounds, which are absorbed by the charcoal.

(*d*) Some *Iodides*, *Bromides*, *Chlorides*, and *Sulphides* are volatilized without reduction, and may form a white or gray coating on the charcoal, at variable distances from the assay.

(*e*) *Nitrates*, *Chlorates*. Their heating is usually accompanied by deflagration.

B. SOLUTION AND SYSTEMATIC ANALYSIS.

1a. Reduce a quantity of the substance to a fine powder in a mortar and treat in the following manner: —

a. Put a pinch of the powder into a test-tube with about ten times its bulk of cold water, and shake thoroughly for a minute. If the substance does not dissolve, boil for a few minutes. If it dissolves completely in either hot or cold water, treat a larger portion of the powder in the same way, and test for *Bases* by Experiment 40, and for *Acids* by Experiment 67.

b. If only a part of the substance dissolves in **a**, as may be determined by evaporating a few drops of the liquid on platinum foil, decant or filter, and test the filtrate by Experiments 40 and 67. Reserve the residue for *c*.

c. That portion of the solid insoluble in water should be treated successively and separately, as far as may be necessary to effect solution, first with dilute and then concentrated hydrochloric acid, dilute and concentrated nitric acid, and aqua regia, having them first cold and then boiling, and diluting with water subsequent to the treatment with each concentrated acid. Test the filtrate after each treatment by evaporating a few drops on platinum foil, to determine whether anything has gone into solution, and save or reject the filtrate accordingly. The hydrochloric acid, nitric acid, and aqua regia solutions should separately be evaporated nearly to dryness, redissolved in water, with the addition of a little free acid if necessary, and analyzed for *Bases* and *Acids* according to Experiments 40 and 67.

d. Fusion with Alkali Carbonates. — If the substance is insoluble, or *only partly* soluble in water or acids, mix one part of it by weight with four or five parts each of sodium and potassium carbonates, and heat in a platinum crucible (or on foil) until the mass is in a state of quiet fusion, when the crucible should be placed on a cold iron plate to cool. If free sulphur is present, it should be removed before fusion by heating the substance in a covered porcelain crucible until the sulphur is expelled. If the Preliminary Examination revealed the presence of lead or silver or other easily reduced metal, a porcelain crucible should be substituted for platinum, since otherwise the vessel will be ruined through the formation of an easily fusible alloy. The fused mass may usually be removed from the crucible in a cake, and should be soaked in boiling water until everything soluble has dissolved. Filter. Treat the filtrate as directed in **e**. The residue contains the bases as carbonates. Thoroughly wash it, and then dissolve in hot dilute hydrochloric acid (or in the presence of silver or lead, nitric acid), evaporate to dryness, ignite, redissolve in boiling dilute hydrochloric acid (or nitric acid), and examine for *Bases* as directed in Experiment 40. A residue insoluble in hydrochloric acid (or nitric acid) is *Silica*. Since sodium and potassium were added in the flux, this solution should not, of course, be used in making a test for those metals.

e. The filtrate from **d** contains such *Acids* as were present in the substance decomposed by the fusion, and also such *Bases* as are soluble in strong alkalies.

(*a*) Acidulate a portion of the filtrate with hydrochloric acid and test for *Sulphates*, as in Experiment 43 (*a*).

(*b*) Acidulate a second portion with acetic acid, and test for *Chromates* as in Experiment 54 (*a*).

(*c*) Acidulate a third portion with nitric acid, and test for *Chlorides* as in Experiment 57 (*b*).

(*d*) Acidulate a fourth portion with nitric acid, and test for *Phosphates* as in Experiment 44 (*a*).

If the test indicates *Arsenates*, remove them with hydrogen sulphide, boil off the excess of the reagent, add nitric acid, heat, and test again for *Phosphates*.

(*e*) Acidulate the remainder of the filtrate with hydrochloric acid, evaporate to dryness, and ignite. Digest the residue with boiling dilute hydrochloric acid. If an insoluble residue remains, it is *Silica*. Filter, and examine the hydrochloric acid solution for *Bases* as in Experiment 40.

NOTES AND SUGGESTIONS.

1. The acid solvents should be used in the exact order indicated in **c** unless the Preliminary Examination revealed the presence of *lead*, *silver*, or *mercury*, in which case nitric acid should be used before hydrochloric acid.
2. Four or five times as much acid should be used in **c** as the bulk of the solid to be dissolved, and the heating should be reasonably prolonged. If there is the slightest doubt as to the solubility of a residue, add a fresh quantity of the acid, and repeat the operation.
3. It is usually unnecessary to look for first group metals in the hydrochloric acid or aqua regia solutions.
4. It is advised in **c** to add water after each treatment with concentrated acid. It is frequently the case that while a strong acid is required to attack a substance, the product formed is soluble only in the dilute acid or in water. Substances separating out of the solution upon dilution are to be treated as insoluble.
5. If a residue remains in **c** after treatment with hydrochloric acid, it should be well washed before digesting with nitric acid.
6. **Special Tests.** — A substance insoluble in water or acids is likely to be either a chloride of lead or silver; a sulphate of lead, barium, calcium, or strontium; an anhydrous or ignited sesquioxide of iron, aluminum, or chromium; binoxide of tin; sulphur or carbon; chrome iron ore; silica or a silicate; or fluoride of calcium. Much time may frequently be saved by testing directly for these substances before resorting to fusion. The most important of these tests are as follows: —

   (*a*) Repeat the closed-tube test upon a small portion of the residue, looking especially for *sulphur*.

   (*b*) Heat a portion on platinum foil. If either *carbon* or *sulphur*, it will be consumed; in the case of the latter, burning with a blue flame. *Graphite* will not burn, but may be recognized by its peculiar adhesive property.

   (*c*) *Silica* may be tested for as instructed in Note 7.

   (*d*) Lead chloride may be dissolved by using sufficient water and boiling. Test the solution as in Experiment 1 (*d*).

   (*e*) Heat a small sample of the residue with a concentrated solution of ammonium acetate, acidulated with a few drops of acetic acid. If lead sulphate is present, it will be dissolved. Filter. Test a portion of the filtrate for *lead* by adding sulphuric acid in excess, and another portion for *sulphates* as in Experiment 43.

(*f*) Repeat the reduction test (p. 211) on some of the residue, looking especially for *lead*, *silver*, and *tin*.

(*g*) Test some of the substance for *fluorides*, as follows: Fuse the material with five times its bulk of sodium carbonate, boil the fused product with water, and filter. Acidulate with acetic acid. If a precipitate forms, filter it off. To the filtrate add solution of calcium chloride, $CaCl_2$, and allow to stand for some time. Collect the precipitate on a small filter, dry, and test for *fluorine* as instructed in Experiment 47 (*a*).

7. **Test for Silica.** — If a portion of the fused mass in **d** refuses to dissolve in hydrochloric acid, it may consist of *silica* or of some of the original substance which was undecomposed by the fusion. Test it by putting it into a platinum crucible, adding 1 or 2 cc. of hydrofluoric acid, and evaporating to dryness. If the substance is pure *silica*, complete volatilization will take place. The operation should be conducted under a hood, and every precaution taken to avoid inhaling the hydrofluoric acid gas or having it come in contact with the skin.

8. **Fusion with Sodium Disulphate.** — For chromic iron ore, ferric oxide, and aluminates the following method of fusion is preferable: —

Mix one part of the finely powdered mineral with four parts of sodium disulphate in a platinum crucible, and apply heat for fully half an hour, at first gently, then raising it until the mixture fuses to a thin liquid. Add two parts of sodium carbonate, and fuse. Cautiously add two parts of sodium nitrate, and after a few minutes increase the heat, stirring meanwhile with a platinum wire. Treat the fused mass as in **d**.

9. **Decomposition with Calcium Carbonate.** — In case *sodium* and *potassium* are to be looked for in the insoluble substance, some method of fusion must be used for a separate portion that does not require a flux containing those elements: —

Prepare an intimate mixture of one part of the finely powdered substance, eight parts of pure calcium carbonate, and one part of ammonium chloride, and heat strongly in a platinum crucible for about an hour. Put the crucible and contents into a beaker containing water, which should be kept at the boiling point for half an hour. Filter. The filtrate contains calcium hydroxide and the chlorides of calcium, sodium, and potassium. Add a small quantity of ammonium hydroxide and then ammonium carbonate in slight excess. Heat *gently* for some time, and filter. Test the filtrate with a drop of ammonium carbonate. If a precipitate forms, repeat the addition of ammonium hydroxide and ammonium carbonate until all the calcium is precipitated, and filter again. Evaporate to dryness, ignite *gently* to expel the ammonium salts, and test the residue for *sodium* and *potassium* as in Experiments 36 (*b*) and (*c*) and 37 (*b*).

10. If the aqueous solution in **a** or **b** gives an acid test with litmus, it may be due to free acids or to salts having an acid reaction. If alkaline, it indicates the presence of a *carbonate*, *phosphate*, *borate*, *sulphide*, or *hydroxide*.

11. In practice it will frequently be found advantageous to combine the aqueous and acid solutions for analysis. This cannot be done, however, if they precipitate each other. Try mixing small portions of the solutions, and note the result.

12. **Removal of Organic Substances.**—The analytical course laid down in this manual does not provide against interference by *organic bodies*. If the Preliminary Examination shows the presence of such matter in any considerable quantity, it must be destroyed before proceeding. Exceptionally, this may be deferred until after the elimination of the first two groups of metals. Unfortunately, there is no method for removing *organic compounds* that is not open to some objection, and the one employed should depend somewhat upon the nature of the substance under examination.

(*a*) Where the amount of *organic matter* is small, simple ignition at a red or white heat is usually sufficient. The combustion should be conducted in a crucible, heating it gently at first, and then strongly until all charring disappears. This operation will exclude the analysis for *mercury*, *arsenious*, *antimonious*, and *ammonium compounds*, all of which are volatilized. *Iron*, *aluminum*, and *chromium* are likely to be changed in part into the insoluble sesquioxides, and if chlorides are present, some *iron*, *sodium*, and *potassium* will be lost through volatilization.

(*b*) If the proportion of *organic matter* is large, it will be better to employ the method advised on page 124, remembering, however, that the changes due to ignition will be even more pronounced through the oxidizing action of the nitric acid.

(*c*) In order to insure against loss of any of the metals (except *ammonium*) and at the same time to wholly remove the *organic matter*, the substance must be submitted to the action of sulphuric with nitric acid, at a gradually increasing temperature. The material should be mixed with equal parts of concentrated sulphuric and nitric acids, and heated on the water-bath for at least fifteen minutes. Then place it over a lamp, and gradually increase the heat until the sulphuric acid begins to vaporize. Cool. Add a small portion of nitric acid, and heat again. Repeat the process, if necessary, until the sulphuric acid becomes light colored. Finally, dilute with water, boil to expel sulphur dioxide, and filter. By this method, *barium*, *calcium*, *strontium*, and *lead* are changed into the insoluble sulphates. Any residue, therefore, should be treated as provided for insoluble substances on page 213.

(*d*) For the removal of fatty matter, ether is ordinarily employed, the substance being treated with two or three successive portions of the solvent. Resinous material may be submitted to the action of alcohol, or both alcohol and ether may be used successively.

SECTION II.

THE SUBSTANCE IS A LIQUID.

I. The Liquid volatilizes without a Residue.

Test the liquid with litmus paper, and evaporate a few drops of it to dryness to determine whether it actually contains any solid matter in solution. If no residue remains, the fluid may be pure water or some other volatile liquid, as alcohol, ether, benzene, ammonia water, or free acid. The odor and litmus test will help determine this point. If an acid, examine as directed in Experiment 67.

II. A Residue remains after Evaporation.

A. THE SOLUTION IS NEUTRAL OR ACID.

a. Examine a portion of the liquid for *Bases* as directed in Experiment 40, and another portion for *Acids*, according to Experiment 67.

B. THE SOLUTION IS ALKALINE.

a. Carefully neutralize or slightly acidulate a portion of the liquid with nitric acid, and examine for *Bases* and *Acids* as in Experiments 40 and 67. If a precipitate forms on neutralization, filter it out and examine separately as directed for *Solids* in Section I. (II.).

NOTES AND SUGGESTIONS.

1. Before proceeding to the regular course of analysis, it is often of material advantage to evaporate a portion of the liquid to dryness, and subject it to the Preliminary Examination as directed in Section I. (II.).
2. It is worth remembering that if the solution is acid, neither sulphides nor carbonates can be present.
3. If the solution is aqueous and neutral, only such substances can be present as are soluble in water.
4. The alkalinity of a liquid may be due to the carbonates, sulphides, cyanides, or hydroxides of barium, calcium, strontium, magnesium, sodium, potassium, or ammonium; or to a phosphate, borate, silicate, arsenate, arsenite or aluminate of potassium or sodium. When the alkalinity is neutralized with an acid, such substances as may be present and require an alkaline solvent will be precipitated. Among these are chloride of silver, silicic acid, sulphides of arsenic, antimony, and tin, and free sulphur.

APPENDIX A.

PREPARATION OF REAGENTS.

THE general use of commercial acids and salts in the preparation of reagents is thought by the author to be an unwise practice, except in such cases as require the most rigid economy. The difficulties in the way of securing convincing results are already sufficiently pronounced without augmenting them through the introduction of unknown extraneous substances. The experienced instructor will know in what instances it is safe to substitute the commercial preparations for the chemically pure. Distilled water should habitually be used in making solutions.

SOLUTIONS.

ACIDS.

Acetic, $HC_2H_3O_2$. — Use the ordinary commercial acid (sp. gr. 1.04) or mix glacial acetic acid with 2½ times its own volume of water.

Aqua Regia. — Mix 1 part of concentrated nitric acid with 3 parts of hydrochloric acid. A different proportion may be needed in specific cases. Prepare as needed only.

Carbolic. — Use the pure white crystals. Handle with care, as it is intensely corrosive and poisonous.

Hydrochloric, HCl. — *Concentrated*, sp. gr. 1.2.

Dilute. — Mix 1 volume of the concentrated acid with 4 volumes of water.

Nitric, HNO_3. — *Concentrated.* The colorless commercial acid of sp. gr. 1.42 is good enough for many purposes in qualitative analysis. When diluted with 5 parts of water, the acid should give no cloudiness with barium nitrate or with silver nitrate. It is safer, ordinarily, to use the c. p. acid.

Dilute.—Add 5 volumes of water to 1 volume of the strong acid.

Sulphuretted Hydrogen Gas, H_2S.—It is prepared through the action of dilute hydrochloric acid upon fragments of iron sulphide, using a gas-generator for the purpose. The apparatus should be placed either in a hood or in the open air.

Sulphuretted Hydrogen Water.—Purify the gas by passing it through a wash-bottle, and conduct it into cold water to saturation. As the solution readily decomposes, only a small quantity should be prepared at a time, and it should be kept in tightly stoppered bottles. Its quality may be determined by cautiously smelling it or by adding a drop of it to a drop of lead acetate, which should immediately blacken.

Sulphuric, H_2SO_4 — *Concentrated*, sp. gr. 1.84.

Dilute. — Gradually and *cautiously* add 1 volume of the concentrated acid to 5 volumes of water, stirring constantly with a glass rod.

Tartaric, $H_2C_4H_4O_6$. — Dissolve 1 part of the powder in 3 parts of hot water.

MMONIUM SALTS.

Acetate, $NH_4C_2H_3O_2$. — Dissolve 1 part of the crystallized salt in 10 parts of water.

Carbonate, $(NH_4)_2CO_3$. — Dissolve without heating 1 part of the acid carbonate of commerce in 4 parts of water, and add 1 part of strong ammonia water. Filter, and keep tightly stoppered in bottles free from lead. As a solvent for arsenious sulphide, it is prepared by dissolving the salt in cold water and omitting the addition of ammonium hydroxide.

Chloride, NH_4Cl. — Dissolve without heating 1 part of the commercial salt in 8 parts of water; let it stand for a day or two, and filter.

Hydroxide, NH_4OH. — *Concentrated*, sp. gr. 90.

Dilute. —Add 2 volumes of water to 1 volume of the strong aqua ammonia. It should be free from carbonic acid, and ought not to give a precipitate with lime water.

Molybdate. — $(NH_4)_2MoO_4$. — Dissolve 30 g. of the dry salt in 200 cc. of dilute ammonium hydroxide, and then cautiously pour this into a mixture of 75 cc. conc. nitric acid and 125 cc of water.

Oxalate, $(NH_4)_2C_2O_4$. — Dissolve one part of the crystallized salt in 24 parts of water, and filter if necessary.

Sulphate, $(NH_4)_2SO_4$. — Dissolve 1 part of the salt in 30 parts of water.

Sulphide, $(NH_4)_2S$. — Pass purified hydrogen sulphide gas into 600 cc. of *dilute* ammonium hydroxide to saturation, and then add sufficient dilute ammonium hydroxide to make up to 1000 cc. It should be prepared in small quantities only, as it decomposes rather readily.

Sulphide (yellow), $(NH_4)_2S_x$. — The sulphide as prepared above will change into the *yellow* form upon exposure to the light and air. To make it directly, digest ammonium sulphide with sufficient sulphur to impart a deep yellow color.

BARIUM SALTS.

Chloride, $BaCl_2$. — Dissolve 1 part of the crystallized salt in 10 parts of water. Filter if not clear.

Hydroxide, $Ba(OH)_2 \cdot 8H_2O$. — Make a saturated aqueous solution.

CALCIUM SALTS.

Chloride, $CaCl_2$. — Dissolve 1 part of the salt in 5 parts of water. Let stand a day, and filter if not clear.

Hydroxide (lime water), $Ca(OH)_2$. — Slake some quicklime in an open iron or tin vessel and add in excess to a large bottle of water. Cork tightly, and shake at frequent intervals for several days. Siphon off the clear liquid into smaller bottles for use.

Sulphate, $CaSO_4 \cdot 2H_2O$. — Make a saturated aqueous solution.

CHLORINE WATER, $Cl + Aq$. — Drop a little concentrated hydrochloric acid on a crystal of potassium chlorate, in a test tube. After vigorous action has begun, add 10 or 15 cc. of water ; or, conduct chlorine gas into cold water to saturation. Since the solution is quite unstable, it should be prepared as needed.

COBALT NITRATE, $Co(NO_3)_2$. — See p. 226.

FERRIC CHLORIDE, $FeCl_3$. — See p. 227.

FERROUS SULPHATE, $FeSO_4$ — See p. 227.

HYDROCHLOROPLATINIC ACID, H_2PtCl_6. — Dissolve 1 part of the crystals in 12 parts of water.

HYDROGEN PEROXIDE, H_2O_2. — Use a 3 per cent solution.

INDIGO SOLUTION. — (1) Dissolve 1 part of commercial indigo paste in 1000 cc. of water. (2) Pour 25 cc. of fuming sulphuric acid into a beaker, and stir into it, little by little, 5 g. of powdered commercial indigo. Let it stand two or three days, and then cautiously add to 1000 cc. of water.

LEAD ACETATE, $Pb(C_2H_3O_2)_2$. — Dissolve 1 part of the salt in 10 parts of water. Let it stand a day, and then filter if not clear.

MAGNESIA MIXTURE. — In 80 cc. of water dissolve 10 grams of magnesium sulphate, $MgSO_4$, 20 grams of ammonium chloride, NH_4Cl, and 40 cc. of ammonium hydroxide.

MERCURIC CHLORIDE, $HgCl_2$. — Dissolve 1 part of the salt in 16 parts of water. It is a violent poison.

POTASSIUM SALTS.

Acetate, $KC_2H_3O_2$. — Use a saturated solution.

Chromate, K_2CrO_4. — Dissolve 1 part of the salt in 10 parts of water.

Cyanide, KCN. — Dissolve 1 part of the pure salt in 4 parts of cold water, and keep in a *plainly labelled* bottle. As it is a *violent poison*, the utmost caution should be exercised in handling it.

Dichromate, $K_2Cr_2O_7$. — Dissolve 1 part of the pure crystallized salt in 10 parts of water.

Ferricyanide, $K_3Fe(CN)_6$. — Dissolve 1 part of the salt in 10 parts of cold water. Since the solution undergoes decomposition rather readily, it is best to prepare it as needed.

Ferrocyanide, $K_4Fe(CN)_6$. — Dissolve 1 part of the salt in 12 parts of water.

Hydroxide, KOH. — Use the pure stick form, and dissolve in 10 parts of water. It should be kept in tightly stoppered bottles, free from lead, and preferably provided with caoutchouc stoppers.

Iodide, KI. — Dissolve 1 part of the pure salt in 20 parts of water.

Nitrate, KNO_3. — Dissolve 1 part of the salt in 10 parts of water.

Nitrite, KNO_2. — Dissolve 1 part of the salt in 10 parts of water. Since it oxidizes readily, the solution should be prepared only as needed.

Permanganate, $KMnO_4$. — Dissolve 5 parts of the crystals in 1000 parts of water.

Stannite, K_2SnO_2. — Prepare as needed by adding to a stannous chloride solution, in a test tube, sufficient potassium hydroxide to redissolve the precipitate at first formed.

Sulphate, K_2SO_4. — Dissolve 1 part of the salt in 12 parts of water. For some purposes it is necess [illegible] ate solution, containing 1 part of the salt to 200 pa

Thiocyanate, KCNS. — Dissolve 1 part of the salt in 10 parts of water.

SILVER SALTS.

Nitrate, $AgNO_3$. — Dissolve 1 part of the salt in 100 parts of water.

Sulphate, $AgSO_4$. — Use a saturated solution.

SODIUM SALTS.

Acetate, $NaC_2H_3O_2$. — Dissolve 1 part of the crystallized salt in 10 parts of water.

Carbonate, Na_2CO_3. — Dissolve 1 part of the pure crystals, at least free from sodium sulphate, in 3 parts of water; or, dissolve 1 part of the anhydrous salt in 5 parts of water.

Hydroxide, NaOH. — Use the pure stick form, and dissolve in 10 parts of water. It should be kept in tightly stoppered bottles, free from lead, and preferably provided with caoutchouc stoppers.

Nitroprusside, $Na_2FeNO(CN)_5$. — Dissolve 1 part of the salt in 10 parts of water.

Phosphate, Na_2HPO_4. — Dissolve 1 part of the crystallized salt in 10 parts of water.

Sulphite, Na_2SO_3. — Dissolve 1 part of the salt in 5 parts of water.

STANNIC CHLORIDE, $SnCl_4$. — Dissolve 1 part of the salt in 30 parts of water.

STANNOUS CHLORIDE, $SnCl_2$. — Dissolve 1 part of the salt in 5 parts of water strongly acidulated with hydrochloric acid.

STARCH PASTE. — Prepare as needed by rubbing 1 part of starch with sufficient cold water to reduce to the consistence of cream, and pouring into 500 parts of boiling water. Use when cold.

ZINC NITRATE, $Zn(NO_3)_2$. — See p. 229.

SOLVENTS.

ALCOHOL, Amyl. — The c.p. liquid should be used in the fifth group separation.

ALCOHOL, C_2H_6O. — Use the commercial liquid (sp. gr. .815), containing 95 per cent of alcohol, unless otherwise directed.

BENZOL. — Use the c.p. liquid.

CARBON DISULPHIDE, CS_2. — Use the commercial article. Handle with the utmost care, since it is highly combustible, and a mixture of its vapor with air is violently explosive.

THER, $(C_2H_5)_2O$. — Use the ordinary commercial ether.

THER-ALCOHOL. — Mix 1 volume of absolute ether with 1 volume of absolute alcohol.

ATER. — Use distilled water or *clean* rain water.

DRY REAGENTS.

EAD PEROXIDE, PbO_2. — Only the c.p. oxide should be used.

ITMUS PAPER. — The paper now on the market is so inexpensive and of such good quality that it is poor economy for the smaller laboratories to attempt to prepare it. Purchase in sheets, cut into slips, and keep in tightly closed bottles.

ANGANESE DIOXIDE, MnO_2. — Use the artificial peroxide.

ICROCOSMIC SALT, $HNaNH_4PO_4$. — Pulverize the commercial crystals, and keep for use.

OTASSIUM CYANIDE, KCN. — The pure granulated form is the best for most purposes. It should be kept in a tightly stoppered bottle, and plainly labelled. Handle with care.

OTASSIUM CHLORATE, $KClO_3$. — Use the c. p. crystals.

OTASSIUM IODIDE, KI. — The commercial crystals may be used.

OTASSIUM NITRATE, KNO_3. — The refined saltpeter may be used. Keep it in the form of powder.

ODIUM SALTS.

Carbonate, Na_2CO_3. — Use the crystals or the pure dry powder as the directions require.

Peroxide, Na_2O_2. — Use the c.p. oxide.

Tetraborate, $Na_2B_4O_7 . 10\ H_2O$. — Use common *borax*, powdered.

URMERIC PAPER. — Cut into slips and keep in tightly closed boxes or dark colored bottles away from light and fumes.

APPENDIX B.

SOLUTIONS FOR ANALYSIS.

THE solutions made of the strengths here indicated are intended, in the main, to be used as *stock* solutions. Before putting them into the hands of the students they should be diluted with from two to ten times their volume of water, or sufficient to reduce the proportion of solid to 1% or 2%.

ALUM (potassic alum), $AlK(SO_4)_2$. — Dissolve 1 part of the commercial crystals in 10 parts of water.

ALUMINUM CHLORIDE, $AlCl_3$. — Dissolve 1 part of the crystallized salt in 10 parts of water.

AMMONIUM ACETATE, $NH_4C_2H_3O_2$. — See p. 221.

AMMONIUM FLUORIDE, NH_4F. — Dissolve 1 part of the salt in 10 parts of water.

AMMONIUM NITRATE, NH_4NO_3. — Dissolve 1 part of the crystallized salt in 10 parts of water.

BARIUM NITRATE, $Ba(NO_3)_2$. — Dissolve 1 part of the crystallized salt in 15 parts of water.

BISMUTH NITRATE, $Bi(NO_3)_3$. — Dissolve 1 part of the crystallized salt in 10 parts of dilute nitric acid, and add 20 parts of water.

CADMIUM NITRATE, $Cd(NO_3)_2$. — Dissolve 1 part of the crystallized salt in 10 parts of water.

CALCIUM NITRATE, $Ca(NO_3)_2$. — Dissolve 1 part of the crystallized salt in 10 parts of water.

CHROMIUM SULPHATE, $Cr_2(SO_4)_3$. — Dissolve 1 part of the salt in 10 parts of water. Chrome alum, $CrK(SO_4)_2$, can usually be substituted, and the solution is prepared in the same proportions.

COBALT NITRATE, $Co(NO_3)_2$. — Dissolve 1 part of the commercial salt in 10 parts of water, and filter it if not clear.

Copper Nitrate, $Cu(NO_3)_2$. — Dissolve 1 part of the crystallized salt in 10 parts of water.

Copper Sulphate, $CuSO_4$. — Dissolve 1 part of the crystallized salt in 10 parts of hot water.

Ferric Chloride, $FeCl_3$. — Dissolve 1 part of the pure salt in 15 parts of water.

Ferrous Sulphate, $FeSO_4$. — Dissolve 1 part of the pure crystallized salt in 10 parts of water, and keep in a closely stoppered bottle. As it oxidizes readily, it should be prepared in small quantities as needed. If necessary to preserve it, place scraps of iron in the solution, and add a drop or two of concentrated sulphuric acid every day.

Ferrous Sulphide, FeS. — Use the commercial sticks.

Lead Nitrate, $Pb(NO_3)_2$. — Dissolve 1 part of the salt in 10 parts of water.

Lead Nitrite, $Pb(NO_2)_2$. — Dissolve 1 part of the salt in 10 parts of water.

Magnesium Nitrate, $Mg(NO_3)_2$. — Dissolve 1 part of the crystallized salt in 10 parts of water.

Manganese Nitrate, $Mn(NO_3)_2$. — Dissolve 1 part of the salt in 10 parts of water.

Mercuric Nitrate, $Hg(NO_3)_2$. — Dissolve 1 part of the salt in 10 parts of water that has been strongly acidulated with nitric acid.

Mercurous Nitrate, $HgNO_3$. — Dissolve 1 part of the crystallized salt in 20 parts of distilled water, and add 1 part of concentrated nitric acid. Keep in a bottle containing a small quantity of metallic mercury.

Nickel Nitrate, $Ni(NO_3)_2$. — Dissolve 1 part of the crystallized salt in 10 parts of water.

Oxalic Acid, $C_2H_2O_4$. — Dissolve 1 part of the crystals in 10 parts of water.

Potassium Antimony Tartrate (tartar emetic), $KSbOC_4H_4O_6$. — Dissolve 1 part of the commercial salt in 10 parts of water.

Potassium Bromide, KBr. — Dissolve 1 part of the crystallized salt in 20 parts of water.

Potassium Chlorate, $KClO_3$. — Dissolve 1 part of the salt in 25 parts of water.

Potassium Cyanide, KCN. — Dissolve 1 part of the salt in 10 parts of water.

POTASSIUM IODIDE, KI. — Dissolve 1 part of the crystallized salt in 20 parts of water.

POTASSIUM NITRATE, KNO_3. — Dissolve 1 part of the crystallized salt in 10 parts of water.

POTASSIUM NITRITE, KNO_2. — Dissolve 1 part of the salt in 10 parts of water.

SILVER NITRATE, $AgNO_3$. — Dissolve 1 part of the commercial crystals in 20 parts of distilled water, and let stand for twenty-four hours. If not clear, siphon off or filter through glass wool. Keep closely stoppered.

SODIUM ACETATE, $NaC_2H_3O_2$. — See p. 224.

SODIUM ARSENATE, Na_3AsO_4. — Dissolve 1 part of the pure salt in 10 parts of water.

SODIUM ARSENITE, Na_3AsO_3. — Dissolve 1 part of the pure salt in 20 parts of water.

SODIUM CARBONATE, Na_2CO_3. — Dissolve 1 part of the anhydrous salt in 10 parts of water.

SODIUM CHLORIDE, NaCl. — Dissolve 1 part of common salt in 10 parts of water. Filter.

SODIUM NITRATE, $NaNO_3$. — Dissolve 1 part of the crystallized salt in 10 parts of water.

SODIUM PHOSPHATE, Na_2HPO_4. — Dissolve 1 part of the crystallized salt in 10 parts of water.

SODIUM SILICATE, Na_2SiO_3. — Purchase in the form of solution (water glass) or dissolve 1 part of the crystallized salt in 10 parts of water.

SODIUM SULPHATE, Na_2SO_4. — Dissolve 1 part of the crystallized salt in 10 parts of water.

SODIUM SULPHIDE, Na_2S. — Dissolve 1 part of the salt in 8 parts of water.

SODIUM SULPHITE, Na_2SO_3. — Dissolve 1 part of the crystallized salt in 10 parts of water.

SODIUM TETRABORATE (borax), $Na_2B_4O_7$. — Dissolve 1 part of the refined crystals in 10 parts of water.

SODIUM THIOSULPHATE, $Na_2S_2O_3$. — Dissolve 1 part of the crystals in 10 parts of water.

SODIUM and POTASSIUM TARTRATE (Rochelle Salts), $NaKC_4H_4O_6$. — Dissolve 1 part of the crystallized salt in 10 parts of water.

STANNOUS CHLORIDE, $SnCl_2$. — (1) Dissolve 1 part of the commercial salt in 10 parts of water acidulated with hydrochloric acid. Keep in a tightly closed bottle containing some granulated tin.

(2) Dissolve granulated tin in hot concentrated hydrochloric acid, making sure that the tin is in excess. Dilute with four times its bulk of water acidulated with hydrochloric acid. Keep some granulated tin in the solution.

STRONTIUM NITRATE, $Sr(NO_3)_2$. — Dissolve 1 part of the crystallized salt in 10 parts of water.

ZINC NITRATE, $Zn(NO_3)_2$. — Dissolve 1 part of the crystallized salt in 10 parts of water.

CARE OF PLATINUM CRUCIBLES.

The use of platinum vessels is almost indispensable at certain stages of analytical operations. They respond so readily to the temperature of the flame in which they are placed and are so secure from the attack of most fluxes and other reagents that they have found a wide and general use in the chemical laboratory. Their expensiveness and delicacy, however, necessitate handling them with the utmost care, and their durableness will depend largely upon the observance of the following precautions: —

1. The oxidizing flame only should be allowed to come in contact with the vessel.
2. Do not heat nor cool the crucible too quickly. The sudden expansion or contraction is liable to crack it.
3. Never heat in it any readily fusible metal (silver, lead, mercury, arsenic, antimony, tin, bismuth, copper), or any oxide or salt or mixture of substances from which such metals could be obtained by reduction, for it would then be ruined through the formation of fusible alloys.
4. Phosphates, in the presence of organic matter, the sulphides, cyanides, hydroxides, and nitrates of the alkali metals, and any solution evolving chlorine, as aqua regia, will attack platinum, and as a rule should not be heated in such vessels.
5. The shape of the crucible may best be preserved by keeping it on a wooden plug when not in use.
6. Clean and polish after using. This may be done by scouring with fine moist sea sand. Boiling hydrochloric or nitric acid in it, or heating with sodium carbonate or bisulphate of potash, are helpful means of removing stains, and will save excessive rubbing.

APPENDIX C.

TABLE OF ATOMIC WEIGHTS.

The values here given are based upon Oxygen = 16, in accordance with the Eighth Report of the Committee on Atomic Weights. The "approximate" list gives the values used in all ordinary calculations.

Name.	Symbol.	Approximate Value.	Accurate Value.
Aluminum	Al	27	27.1
Antimony	Sb	120	120.4
Argon	Ar	40	40?
Arsenic	As	75	75
Barium	Ba	137	137.4
Bismuth	Bi	208	208.1
Boron	B	11	11
Bromine	Br	80	79.95
Cadmium	Cd	112	112.4
Cæsium	Cs	133	132.9
Calcium	Ca	40	40.1
Carbon	C	12	12
Cerium	Ce	139	139
Chlorine	Cl	35.5	35.45
Chromium	Cr	52	52.1
Cobalt	Co	59	59
Columbium	Cb	94	93.7
Copper	Cu	63.5	63.6
Erbium	Er	166	166
Fluorine	F	19	19.05
Gadolinium	Gd	157	157
Gallium	Ga	70	70

NAME.	SYMBOL.	APPROXIMATE VALUE.	ACCURATE VALUE.
Germanium	Ge	72.5	72.5
Glucinum	Gl	9	9.1
Gold	Au	197	197.2
Helium	He	4	4?
Hydrogen	H	1	1.008
Indium	In	114	114
Iodine	I	127	126.85
Iridium	Ir	193	193.1
Iron	Fe	56	55.9
Krypton	Kr	59	59?
Lanthanum	La	138.5	138.6
Lead	Pb	207	206.9
Lithium	Li	7	7.03
Magnesium	Mg	24	24.3
Manganese	Mn	55	55
Mercury	Hg	200	200
Molybdenum . . .	Mo	96	96
Neodymium	Nd	143.5	143.6
Neon	Ne	20	20?
Nickel	Ni	58.5	58.7
Nitrogen	N	14	14.04
Osmium	Os	191	191
Oxygen	O	16	16
Palladium	Pd	107	107
Phosphorus	P	31	31
Platinum	Pt	195	194.9
Potassium	K	39	39.11
Praseodymium . . .	Pr	140.5	140.5
Rhodium	Rh	103	103
Rubidium	Rb	85.5	85.4
Ruthenium	Ru	102	101.7
Samarium	Sm	150	150.3
Scandium	Sc	44	44.1
Selenium	Se	79	79.2
Silicon	Si	28.5	28.4

NAME.	SYMBOL.	APPROXIMATE VALUE.	ACCURATE VALUE.
Silver	Ag	108	107.92
Sodium	Na	23	23.05
Strontium	Sr	87.5	87.6
Sulphur	S	32	32.07
Tantalum	Ta	183	182.8
Tellurium	Te	127.5	127.5?
Terbium	Tr	160	160
Thallium	Tl	204	204.15
Thorium	Th	232.5	232.6
Thulium	Tm	170.5	170.7
Tin	Sn	119	119
Titanium	Ti	48	48.15
Tungsten	W	184	184
Uranium	U	239.5	239.6
Vanadium	V	51.5	51.4
Xenon	X	?	?
Ytterbium	Yb	173	173.2
Yttrium	Y	89	89
Zinc	Zn	65.5	65.4
Zirconium	Zr	90.5	90.4

APPENDIX D.—TABLE OF SOLUBILITIES.

	Aluminium.	Ammonium.	Antimony (ous).	Barium.	Bismuth.	Cadmium.	Calcium.	Chromium.	Cobalt.	Copper (ic).	Gold.	Hydrogen.	Iron (ous).	Iron (ic).	Lead.	Magnesium.	Manganese.	Mercury (ous).	Mercury (ic).	Nickel.	Platinum.	Potassium.	Silver.	Sodium.	Strontium.	Tin (ous).	Tin (ic).	Zinc.
Acetate . . .	W	W	—	W	W	W	W	W	W	W	—	W	W	W	W	W	W	WA	W	W	—	W	W	W	W	W	W	W
Arsenate . . .	A	W	A	A	A	—	A	A	A	A	—	W	A	A	A	A	A	A	A	A	—	W	A	W	A	—	A	A
Arsenite . . .	—	W	A	A	—	—	A	—	A	A	—	W	A	A	A	A	A	A	A	A	—	W	A	W	A	—	—	—
Borate . . .	A	W	—	A	A	WA	A	A	A	A	—	W	A	A	A	WA	A	—	—	A	—	W	A	W	A	A	—	A
Bromide . . .	W	W	WA	W	WA	W	W	W&I	W	W	W	W	W	W	WI	W	W	AI	W	W	W	W	I	W	W	—	—	W
Carbonate . . .	—	W	—	A	A	A	A	—	A	A	—	W	A	—	A	A	A	A	A	A	—	W	A	W	A	—	—	A
Chlorate . . .	W	W	—	W	W	W	W	W	W	W	—	W	W	W	W	W	W	W	W	W	—	W	W	W	W	W	—	W
Chloride . . .	W	W	WA	W	WA	W	W	W&I	W	W	W	W	W	W	WI	W	W	AI	W	W	W	W	I	W	W	W	W	W
Chromate . . .	—	W	A	A	A	A	WA	A	A	W	—	W	—	W	AI	W	W	A	WA	A	—	W	A	W	WA	A	—	W
Cyanide . . .	—	W	—	WA	—	A	W	A	AI	A	W	W	AI	—	A	W	A	—	W	AI	W	W	I	W	W	—	—	A
Ferricyanide .	—	W	—	—	—	—	W	—	I	—	—	W	I	W	WA	W	I	—	—	I	—	W	I	W	—	I	—	A
Ferrocyanide .	—	W	—	WA	—	—	W	—	I	I	—	W	I	I	A	W	A	—	—	I	—	W	I	W	W	I	I	AI
Fluoride . . .	W	W	W	WA	W	WA	AI	W	WA	A	—	W	WA	W	A	AI	A	—	WA	WA	—	W	W	W	WA	W	W	WA
Hydroxide . .	A	W	A	W	A	A	WA	A	A	A	—	W	A	A	A	A	A	—	—	A	—	W	—	W	W	A	A&I	A
Iodide	W	W	WA	W	A	W	W	W	W	W	A	W	W	W	WA	W	W	A	A	W	I	W	I	W	W	W	W	W
Nitrate . . .	W	W	—	W	W	W	W	W	W	W	—	W	W	W	W	W	W	W	W	W	W	W	W	W	W	—	—	W
Oxalate . . .	A	W	A	A	A	A	A	WA	A	A	—	W	A	A	A	A	WA	A	A	A	W	W	A	W	A	A	W	A
Oxide	A	W	AH	W	A	A	WA	A&I	A	A	—	W	A	A	A	A	AH	A	A	A	A	W	A	W	W	A	A&I	A
Phosphate . .	A	W	WA	A	A	A	A	A	A	A	—	W	A	A	A	A	A	A	A	A	—	W	A	W	A	A	A	A
Silicate . . .	AI	—	—	A	—	A	A	A	A	A	—	W	A	A	A	A	A	—	—	A	—	W	—	W	A	—	—	A
Sulphate . . .	W	W	A	I	W	W	WI	W&I	W	W	—	W	W	W	AI	W	W	WA	W	W	W	W	WA	W	I	W	—	W
Sulphide . . .	A	W	AH	W	A	A	WA	AI	A	A	AR	W	A	A	A	A	A	A	A	A	AR	W	AN	W	W	AH	AH	A
Sulphite . . .	A	W	A	A	A	W	W	W	A	W	—	W	W	W	A	W	A	A	A	A	—	W	A	W	A	W	W	W
Tartrate . . .	W	W	A	A	A	WA	A	W	W	W	—	W	WA	W	A	WA	WA	WA	A	A	—	W	A	W	A	A	—	A

W = Soluble in water.
A = Insoluble in water, but soluble in strong acids (HCl, HNO_3, and aqua regia).
AI = Insoluble in water, difficultly soluble in acids.

AH = Insoluble in water, soluble in HCl.
AN = Insoluble in water, soluble in HNO_3.
AR = Insoluble in water, soluble in aqua regia.

I = Insoluble in water, HCl, or HNO_3.
WA = Difficultly soluble in water, but soluble in HCl or HNO_3.

WI = Difficultly soluble in water, the solubility not being greatly increased by the addition of acids.

APPENDIX E.

THEORIES OF SOLUTIONS.

Strictly speaking, it is impossible to give a satisfactory definition of the term "solution." Ostwald says: "Solutions are homogeneous mixtures — mixtures which allow no separation of their components by mechanical means." In this broad sense, a homogeneous mixture of gases or solids is as truly a solution as is the liquid product to which the name is popularly limited. Until within recent years, the conditions under which substances exist in solution were but vaguely understood, and even to-day there is but little exact knowledge concerning this most common and important of physical phenomena. The modern theories and speculations which have grown out of the work of such eminent investigators as Van't Hoff, Arrhenius, Ostwald, Kohlrausch, and Planck, and which are now pretty generally accepted, are certainly of exceeding helpfulness to the student of analytical chemistry, and it is desirable that he should secure a broader acquaintance with them than is possible from the brief outline here presented.

It should be premised that the fundamental idea underlying these conceptions is that substances in solution are in a state comparable to that of gases; or, as stated by Van't Hoff (1886): *The osmotic pressure of a substance in solution is identical with the pressure which it would exert were it in the form of a gas occupying the same volume* (i.e. *the volume of the solution*) *at the same temperature.* As the various phenomena of gases, such as their deportment under changing temperature and pressure, are ascribed to the number of molecules in a specific quantity of the gas, so it seems a justifiable assumption that the osmotic pressure depends upon the number of unit particles of the substance present in the solution, and not upon its chemical properties. In connection with this hypothesis, it has been shown that while sugar and many other bodies of the most diverse nature are in perfect conformity with the law, solutions of acids, bases, and salts appear to contain a larger number of unit particles than can be accounted for by molecular division solely. In order to explain these abnormalities, it was suggested that the substance in solution is broken up into smaller bodies or sub-molecules; but the explanation seemed rather far-fetched until it was seen that this assumption would also throw light upon some other heretofore unexplained phenomena, such as the behavior of solutions when subjected to the passage of an electric current.

It has long been known that there are two distinct ways in which the movement of electricity takes place in bodies. When the current is passed through metallic conductors or carbon, no other change than heating occurs, whereas in the case of aqueous solutions of acids and bases, and of salts, either fused or in solution, decomposition of the substance takes place simultaneously. Faraday suggested that the components of this latter class of conductors, or electrolytes, consist of freely moving particles, some of which are charged with positive, and the others with negative, electricity. To these particles he gave the name *ions*. It is an observed fact that during the transmission of a current by an electrolyte, the hydrogen of the acids, and the metals (or metallic radicals) of the bases and salts, migrate from the positive electrode to the negative; while the hydroxyl of the bases, and the acid radicals or elements, move in an opposite direction. The appearance of decomposition products at the poles is evidence of the movement referred to. If the ions are the carriers of the electric current, then equal quantities of electricity in passing through different electrolytes will require equivalent quantities of ions. In trying to account for apparent deviations from Faraday's electrolytic law, Arrhenius was led to propose his "Theory of Electrolytic Dissociation." In brief, this theory assumes that when an electrolyte is dissolved in water, it is not present as intact molecules, but is more or less dissociated into electrically charged particles, or ions, depending upon the degree of dilution and the nature of the electrolyte. Under ordinary circumstances, the identity of the solution is maintained through the neutralizing effect which ions of opposite polarities exert upon each other; but the moment this equilibrium is disturbed, as, for example, by the passage of an electric current, the ions pass to their respective poles, and are transformed from the ionized condition to the less reactive molecules.

Not only does the Dissociation Theory satisfactorily explain the nature of electrolytic conduction, but also the phenomenon of abnormal osmotic pressure; for, as was demonstrated by Arrhenius in 1887, solutions of non-electrolytes, as sugar, for example, show normal osmotic pressure, whereas electrolytic solutions are precisely those whose osmotic pressure is greater than it ought to be from the calculated molecular weight. In fact the connection between the two properties is so close that from the electric conductivity we can determine the numerical value of the osmotic pressure. Aside from this parallelism, there is a whole series of other phenomena, such as vapor pressure, specific heat, freezing and boiling points of solutions, etc., which were unintelligible until viewed in the light of this theory, but which are now given real meaning and importance.

Applying this theory to analytical methods, it is evident that the tests employed in qualitative analysis are dependent upon reactions with ions and not with molecules, and that unless an element or radical is present in the ionized condition, it is not capable of those activities by which the substance is usually identified. For example, a solution of sodium chloride possesses certain properties which are characteristic of the sodium and chlorine ions, rather than of salt itself, and the chlorine is easily detected by precipitation with silver nitrate. In like manner, the presence of chlorine in all metallic chlorides is revealed by this reagent. But in the case of potassium chlorate ($KClO_3$) and chloroform ($CHCl_3$), the chlorine does not respond to the typical test, since the ions of the former are K and ClO_3, and the latter is non-electrolytic. Silver nitrate, then, is a reagent for chlorine ions, and not for chlorine-containing compounds in general. Again, chromic compounds give with ammonium hydroxide a green precipitate of chromic hydroxide, no matter with what acid radical the chromium may be associated in the molecule; but in chromates and dichromates, where the ions are CrO_4 and Cr_2O_7 respectively, chromium remains unaffected in the presence of ammonium hydroxide. These illustrations can easily be multiplied, and all point to the same conclusion, namely, that the chemical activity of a compound does not depend upon the presence of any particular element, but upon its dissociated ions.

For a fuller discussion of this interesting and important theory, and especially of its application to the details of analytical processes, the student is referred to Ostwald's "Outlines of General Chemistry," and his more recent work, "The Scientific Foundations of Analytical Chemistry," to which the author is largely indebted for this introduction.

APPENDIX F.

SUPPLEMENTARY SCHEME FOR ARSENIC, ANTIMONY, AND TIN.

REMARKS. — Because of the importance of *Arsenic*, *Antimony*, and *Tin* in analytical operations, it seems advisable to introduce an additional scheme for their separation and detection. The following method has been in use in some of the larger laboratories of the country for the past two years, and is highly recommended on account of its accuracy and ease of operation: —

PROCEDURE. — (*a*) Proceed as in Experiment 13 to the point where ammonium carbonate has been added to the precipitate of mixed sulphides. Digest at about 50° for several minutes, and stir well. The arsenic sulphide dissolves. Filter, and acidulate the filtrate with dilute nitric acid. The arsenic sulphide is reprecipitated. Add more nitric acid, as may be necessary, and boil a few minutes. The sulphide dissolves, a little sulphur often remaining visible. Add dilute solution of potassium permanganate, $KMnO_4$, drop by drop, as long as it is quickly decolorized by the boiling liquid. If too much permanganate be added, a brown precipitate may form, which will not disappear on boiling. In this case, add a drop of stannous chloride solution, which will cause the liquid to clear instantly. Add to the clear, colorless, boiling liquid a large excess of ammonium molybdate solution, and allow to stand a few minutes while stirring vigorously. A precipitate of yellow ammonium arseno-molybdate *proves the presence of Arsenic.*

(*b*) The residue insoluble in ammonium carbonate solution should be washed on the filter, and dissolved, by boiling in a porcelain dish with about 5 cc. of concentrated hydrochloric acid, a small crystal of potassium chlorate, and 15 or 20 cc. of water. Boil until all free chlorine is driven off and the liquid is concentrated to 5 or 10 cc. Filter into a side-neck test-tube, which is fitted with a tight stopper and a bent glass delivery tube. Add a piece of sheet zinc, stopper the tube, and *immediately* insert the delivery tube in a test-tube containing about 5 cc. of dilute silver nitrate solution. The evolved gases, consisting of hydrogen and stibine, SbH_3, should bubble through the silver solution for 10 or 15 minutes. The formation of a black precipitate, antimony argentide, $SbAg_3$, *indicates the presence of Antimony.*

$$SbH_3 + 3\,AgNO_3 = SbAg_3 + 3\,HNO_3.$$

(*c*) Separate by filtration the black precipitate obtained in (*b*), and wash until free from undecomposed silver salt. Digest hot with dilute hydrochloric acid. Antimonious chloride, $SbCl_3$, will go into solution, and silver chloride will be left as a precipitate. Remove the excess of acid by evaporation, dilute with a little water, filter, and to the filtrate add hydrogen sulphide. The formation of an orange-colored precipitate, Sb_2S_3, *proves the presence of Antimony.*

(*d*) *Tin*, if present, is deposited in the metallic condition in the generator, and will not redissolve as long as zinc is in excess. The metallic deposit should be treated exactly as advised in Experiment 12, (*c*) and (*d*).

NOTES AND SUGGESTIONS.

1. In case the arsenic is not completely extracted by ammonium carbonate, it will be oxidized to arsenic acid by the free chlorine in (*b*), and upon the addition of the zinc will be changed into the gaseous and *highly poisonous substance* known as *arsine*, AsH_3. Like the analogous compound, stibine, arsine is decomposed by silver nitrate solution; but in this case, black metallic silver is precipitated, *easily mistaken for antimony argentide.* The indication in (*b*), therefore, should always be confirmed by the test in (*c*).

$$AsH_3 + 6\,AgNO_3 + 3\,H_2O = H_3AsO_3 + 6\,Ag + 6\,HNO_3.$$

2. A little silver chloride may be held in solution by the hydrochloric acid in (*c*), in which event a black precipitate will be obtained upon the addition of the hydrogen sulphide. This contingency may be guarded against by adding a drop or two of potassium iodide solution, and filtering off any precipitate formed, after which the filtrate should be tested with hydrogen sulphide for the orange-colored precipitate.

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